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ALIEN PROPERTY CUSTODIAN

METHOD OF CONVERTING HEXYLRESORCINOL INTO AN EASILY WATER SOLUBLE FORM

Helmut Legerlotz, Wien, Austria; vested in the
Alien Property Custodian

No Drawing. Application filed March 31, 1937

Hexylresorcinol, as is well-known, is one of the most powerful antiseptics. However, it has the drawback of being only slightly soluble in water, for which reason its use is out of the question for many purposes.

It has been found that the sulphonic acid of hexylresorcinol, which, as described below, can be prepared in various ways and which forms easily soluble salts with water, far surpasses hexylresorcinol in antiseptic action. Thus, solutions which contain instead of hexylresorcinol, the same quantity of the hexylresorcinol sulphate of potassium are capable of destroying pyocyanus already in 5 minutes instead of 45 minutes. A solution which contains 0.1% of the salt mentioned can immediately destroy pus excitant (staphylococci, streptococci and pyocyanus) and colibacilli. Such an effect was not by any means to be foreseen.

The preparation of the hexylresorcinol sulphonic acid is carried out with almost quantitative yield either by sulphonation of the hexylresorcinol or by reduction of the sulphonic acid formed by treatment of capronyl resorcinol with concentrated sulphuric acid or an other sulphonating agent and will be explained by the following examples:—

Example 1

100 g hexylresorcinol is dissolved in 100 g concentrated sulphuric acid while stirring well. After standing 24 hours, the mass solidified to a crystal paste is dissolved in water and the solution is neutralised with carbonate of lime. By means of potassium carbonate the calcium is precipitated from the liquid filtered from the calcium sulphate, and evaporation to dryness is carried out. The residue constitutes the hexylresorcinol sulphate of potassium.

Example 2

100 g capronyl resorcinol is dissolved in 150 g concentrated sulphuric acid and kept about 8 hours at approximately 60°. After cooling, the crystal mass formed is dissolved in water, the solution is thoroughly treated with ether for the purpose of removing any unchanged capronyl resorcinol, and the aqueous liquid still containing free sulphuric acid is treated at boiling temperature about 6–8 hours with zinc dust while stirring vigorously. After cooling, the major part of the zinc sulphate separates out, and filtering is then carried out. The zinc and the sulphuric acid which is still present are precipitated from the filtrate with a hot solution of caustic baryta and the liquid filtered from the zinc hydroxide and barium sulphate is treated with a potassium carbonate solution in slight excess for the purpose of removing the barium. The filtrate of barium carbonate is brought to dryness.

Example 3

The aqueous solution of hexylresorcinol sulphonic acid still containing sulphuric acid as obtained according to Example 1 is treated with caustic baryta or barium carbonate at boiling temperature until it hardly contains any sulphuric acid, the filtrate is shaken with ether several times for the purpose of removing small quantities of unchanged starting material and then there is dissolved in same (after determination of the degree of acidity) the equivalent quantity of hexamethylenetetramine (1 mol). The residue obtained after the evaporation of the water *in vacuo* constitutes the hexylresorcinol sulfonic acid hexamethyltetramine, which forms compact crystals which easily dissolve in water and dilute alcohol.

HELMUT LEGERLOTZ.

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ALIEN PROPERTY CUSTODIAN

PROCESS FOR OXIDISING UNSATURATED POLYCYCLIC ALCOHOLS

Rupert Oppenauer, Amsterdam, The Netherlands;
vested in the Alien Property Custodian

No Drawing. Application filed May 21, 1937

The chemical investigation of hormones has shown in the last years that a great number of these physiologically and pharmacologically so important substances and particularly the sex-hormones are polycyclic ketones. It has been found e. g. that progesteron which is the active substance of the corpus luteum extracts is Δ -4,5 pregnendion (3,20) and that testosterone is Δ -4,5-androstenol-(17)-on-(3). These and many other hormones which are polycyclic ketones were also prepared by synthetic way from cholesterol, stigmaterol etc. since long, such as, e. g. the progesteron (Butenandt and cooperators Z. Physiol. Chem. 227, 84, 1934, Ber. 67 B, 1611, 2085, 1934 and Fernholz Ber. 67, 1855 2027, 1934), the testosterone (Ruzicka and cooperators Helv. Chim. Acta 18, 1264, 1478, 1935), the methyltestosterone (Ruzicka, Goldberg Rosenberg Helv. Chim. Acta 18, 1487, 1935), the androstendion (Ruzicka, Wettstein, Helv. Chim. Acta 18, 986, 1935) etc.

As starting materials for the preparation of polycyclic ketones such as the above mentioned ones, containing beside a keto-group a double bond substances were used in the already known processes which substances, leaving out of consideration possible sidechains, have a hydroxilic group to C₃ and a double bond between C₅ and C₆. These substances have consequently to undergo during one stage or the other of the synthese the same chemical changes taking place in the preparation of cholestenon from cholesterol.

For effecting this last mentioned reaction two processes have been described. Diels (Ber. 37, 3099, 1904) has melted together cholesterol and cupric oxide at 280-300° C. and obtained in this way cholestenon in a yield of 65%. On the other hand Windaus and Abderhalden (Ber. 39, 518, 1906) added to the double bond of the cholesterol the calculated quantity of bromine, oxidised the dibromide to the dibromoketone by means of KMnO₄ or CrO₃ and then eliminated again the bromine from this dibromoketone; they also obtained in this way a yield of cholestenon of 60 to 65%. Both processes have already been applied for the preparation of polycyclic ketones from alcohols such as e. g. the oxidation by means of CuO according to Diels in connection with the progesteron (Fernholz B. 67, 2030, 1934). In this way, however, only a yield of 4% was obtained which can be readily understood bearing in mind the drastic treatment.

The second process (via the bromine derivatives) is the method generally in use up till now for the synthesis of polycyclic unsaturated ketones. In this way crystallized progesteron e. g.

was obtained from Δ -5, 6-pregnenol-(3)-on-(20) in a yield of 35-40% (Butenandt B. 69, 443, 1936). This method was also applied for the preparation of testosterone and methyl testosterone, however with relatively low yields never exceeding 50% (Ruzicka, loc. cit.). These great losses are due, on the one hand, to the complicated reaction (2 intermediary products) and on the other hand all optimal conditions must be taken into consideration as exactly as possible when executing these reactions, which conditions are, however, different from one case to the other. (vide Butenandt Ber. 67, 2087, 1934), Fernholz (Ber. 67, 2029, 1934).

Other processes for economically effecting the oxidation are unknown up till now. It is true that Schönheimer (J. Biol. Chem. 110, 461, 1935) has described a modification of the last mentioned process in which he obtains cholestenon in a good yield starting from the cholesterol dibromide (the intermediate product of bromination). In this way, however, the losses during the whole reaction are only partly avoided and, moreover, this method is not applicable with the same successful result to substances which may be prepared by my process.

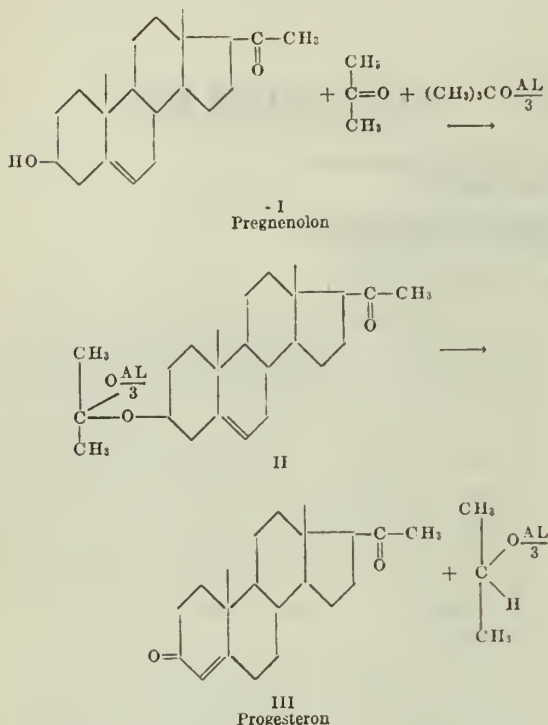
The object of my invention is to effect this oxidation in a completely new and extraordinarily simple way whereby a substantially quantitative yield is obtained. I have found that unsaturated polycyclic alcohols are capable of yielding 2 atoms of hydrogen per molecule and per hydroxilic group to other substances involved in this reaction and containing keto groups under the influence of certain alcoholates. In this way e. g. the compounds of the cholesterol type are oxidised to those of the cholestenon type and as a matter of fact in such a delicate way that the yield is practically the theoretic one.

My new process is in every respect superior to the methods known till now. My process consists herein that the sterol alcohol to be oxidised is treated in presence of tertiary metal alcoholates, preferably tertiary alcoholates of the aluminium or the magnesium chloride with an excess of hydrogen acceptor. Preferably the reaction is carried out at an increased temperature (50-140° C.) in order to increase the reaction speed, and, moreover, in order to increase the solubility of the intermediary reaction products an indifferent solvent, such as benzene may be added.

As hydrogen acceptors I may use ketones and aldehydes of the aliphatic, alicyclic and aromatic series.

Without binding my process to a specific theory

I suppose that the reaction takes place in such a way that from the polycyclic alcohol (I) e. g. with acetone under the action of the aluminium respectively magnesium alcoholate an addition compound (II) is formed which splits into the α,β -unsaturated ketone (III) and propyl alcohol.



My method may be applied to unsaturated polycyclic oxy ketones (e. g. dehydroandrosteron, pregnenolon, etc. which are oxidised in this way to diketones), as well as to unsaturated polycyclic oxi-esters (e. g. the acetate-(17) of the androstendiol) besides to sterol alcohol (e. g. cholesterol). It was particularly surprising that the ester group of the oxi-esters is not saponified during this operation since it was known that esters as a rule react with alcoholates under saponification (vide Windaus and cooperators Ann. 520, 100, 1925). Also the presence of a tertiary OH-group in the molecule is not objectionable in my process so that it is possible to prepare by my method e. g. methyl testosterone from 17-methyl androstendiol-(3,17) in a substantially theoretic yield (compare Ruzicka Helv. Chim. Acta 18, 1487, 1935). By means of my new method special substances can be prepared by synthesis which could not be made up till now, due to the fact that during the drastic oxidation of substances having several double bonds, secondary reactions take place in the known methods. E. g. the ergostatrienon could not yet be prepared till now and its synthesis with a very great yield according to my new process is described in example 5. For carrying the aluminium or magnesium chloride to the hydrocyclic groups to be oxidised, tertiary alcohols come mainly into consideration, such as e. g. trimethyl carbinol, amylene hydrate, triphenyl carbinol.

The progress obtained by my new process consists herein that:

1. The yields are approximately twice as high as in the known processes.

2. The reaction can be effected very simply and requires only a very short reaction time in comparison to the known methods.

3. The method can be applied to crude concentrates with the same success. E. g. a progesteron concentrate can be prepared from the mother liquors of the ketones obtained during the manufacture of the dehydro androsteron from cholesterol or sitosterol and this was technically absolutely impossible till now.

The unsaturated polycyclic ketones prepared in this way may be applied in therapeutics.

My invention is elucidated by but not at all restricted to the following examples:

1. Preparation of cholestenon from cholesterol. 10 grams of cholesterol are dissolved in 100-150 cm^3 of acetone under heating and a solution of 20 grams of tertiary aluminium butylate in 300 cm^3 of anhydrous benzene is added hereto. This mixture is heated under reflux cooling during 7 hours; the aluminium is removed by shaking out with diluted sulphuric acid, the benzene layer is washed with water, dried with sodium sulphate and then evaporated to dryness. Substantially pure cholestenon remains behind which is obtained in crystallized form by recrystallization, e. g. from methanol in a yield of 90-95% of the theory.

2. Preparation of androstendion from dehydroandrosteron, 2 grams of dehydroandrosteron are heated under reflux cooling with 2 grams of aluminate of the amylene hydrate and 80 grams of acetophenone in 150 cm^3 of benzene during 14 hours. One hydrolizes then with diluted sulphuric acid and the washed and dried benzene solution is evaporated to dryness. The residue is fractionally distilled in high vacuum (cathode-vacuum) and the fraction distilling over at 120-140° C. is recrystallized from ether. Androstendion (melting point 170-172° C.) is obtained in a yield of 80-86% of the theory.

3. Preparation of methyl testosterone from methyl androstendiol, 0.6 gram of 17-methyl Δ -5.6 androstendiol (3,17) is heated under reflux cooling during 20 hours in 50 cm^3 of benzene and 12 cm^3 of acetone with 3 grams of tertiary chloro magnesium butylate, which may be prepared by conversion of acetone with methyl magnesium chloride. The further treatment takes place as in Example 1 and methyl testosterone (melting point 160-162° C.) is obtained in a yield of more than 75% of the theory.

4. Preparation of testosterone from androstendiol. 0.7 gram of 17-mono acetate of the androstendiol (3,17) is heated under reflux cooling in 30 cm^3 of toluene and 8 cm^3 of acetone with 1 gram of tertiary aluminium butylate during 5 hours. The further treatment takes place as in Examples 1 and 2 and testosterone acetate (melting point 135-139° C.) is obtained in a yield of 80-90% of the theory.

5. Preparation of ergostatrienon from ergosterol. 1.5 grams of ergosterol are dissolved under heating in 120 cm^3 of gasoline (boiling point 100-125° C.) and heated under reflux cooling after addition of 20 grams of acetone and 1 gram of tertiary aluminium butylate during 8 hours. The further treatment is effected as in Example 1, and 1.12 grams of crystallized ergostatrienon (M. P. 131-132.5° C.) are obtained as needles.

RUPERT OPPENAUER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF NEW EFFICACIOUS P-AMINO-BENZENE-SULPHAMIDE DERIVATIVES, SUITABLE FOR INJECTION PURPOSES

Zoltán Földi, Budapest, Hungary; vested in the Alien Property Custodian

Application filed February 5, 1938

Chemical compounds of the amino-benzene-sulphamide type are extensively used in the therapy, particularly for diseases due to streptococcal infection. However, p-amino-benzene-sulphamide is only to a very slight extent soluble in water and it is therefore unsuitable for preparing solutions of the necessary concentration. Neither are the salts formed by the said compounds with acids, suitable for preparing solutions intended for injection, because their aqueous solutions possess a strong acid effect.

According to our present invention it is possible to obtain p-amino-benzene-sulphamide derivatives readily soluble in water and suitable for injection purposes, if p-amino-benzene-sulphamide, or such derivatives of the same as result from substitutions effected in the nucleus or in the nitrogen atoms are subjected to the action of formaldehyde sulphonylate.

It has been found to be particularly advantageous to perform the reaction of the formaldehyde sulphonylate in the presence of about 1 mol of alkali metal hydroxide, in which case products, extremely soluble in water, are formed, which can be easily isolated from the reaction mixture by addition of mineral acid, whereupon an acid difficultly soluble in water will separate. If this acid is filtered off, washed with water and then neutralized by means of alkali metal hydroxides, as for instance, by sodium hydroxide, an aqueous solution of the product results in which product practically two atoms of sulphur correspond to two atoms of nitrogen i. e. in which product 1 mol of amino-benzene-sulphamide is connected with 1 mol of formaldehyde sulphonylate. Thus for instance 50 grams of p-amino-benzene-sulphamide are dissolved in a mixture of 70 ccm of water and of 20 to 25 ccm of a 47 per cent by volume sodium hydroxide solution by heating in a water-bath, and after cooling a solution of 50 to 100 grams of formaldehyde sodium sulphonylate in 100 to 200 ccm of water is added. This mixture is heated at a temperature of 60 to 80° C during one hour, then the solution is cooled and to the filtered solution hydrochloric acid is added until a filtered test portion will not produce any further precipitate on the addition of hydrochloric acid. The precipitate is collected on a suction funnel, preferably excluding from air, and washed with water. The wet acid gives, neutralised with a solution of sodium hydroxide, a solution of the sodium salt which is easily soluble in water. It is, however, also possible to dry the acid in vacuo over phosphorus pentoxide and to effect the formation of the salt in an alcoholic medium.

If no sodium hydroxide is employed during the action of the sulphonylate, only a very slow reaction will take place between the sulphonylate and the amino-benzene-sulphamides (amino-benzene-sulphamide, benzylamino-benzene-sulphamide, amino-benzene-disulphamide etc.) In this case it will be preferable to employ the sulphonylate in a large excess e. g. two mols of sulphonylate per mol of amino-benzene-sulphamide. Such a reaction mixture has an alkaline reaction, owing to the hydrolysis of the excess of sulphonylate. In this case the heating of the reaction mixture (50 grams of p-amino-benzene-sulphonylamide, 75 grams of formaldehyde sodium sulphonylate, free from water of crystallisation, and 100 ccm. of water) should be continued in a water bath of 70 to 90° C. during about 20 hours. The product formed during this process is likewise most easily soluble in water, but when acidified with mineral acids no free acid will precipitate. The isolation of the product from this reaction mixture is preferably effected by pouring it into a quantity of absolute alcohol amounting to between 6 and 10 times the quantity of the reaction mixture, whereupon the product precipitates in the form of a gummy mass. After allowing the mixture to stand for a while, the liquid is decanted, fresh absolute alcohol is poured to the gummy residue, whereupon the latter becomes converted into a white powdery mass. After drying, a substance very easily soluble in water is obtained; the chemical analysis shows the presence of about 3 atoms of sulphur for each two atoms of nitrogen, i. e. in this product 2 groups of sulphonylate are joined to 1 mol of amino-benzene-sulphamide. The product contains varying amounts of water of crystallisation. About 3 mols of water of crystallisation were found.

The presence of the sulphonylate groups can easily be shown by titration by means of indigo carmine.

The chemical compounds containing two groups of sulphonylate will offer in its aqueous solutions much greater a resistance to the effects of air than the derivatives containing only one sulphonylate group. The reaction of the solutions to litmus is alkaline, but to phenol phthaline practically neutral thus remaining within a reaction range very suitable for solutions intended for injection purpose.

The products of the process are employed for pharmaceutical purposes.

In the present specification the expression "alkali metal" includes also "ammonium."

ZOLTÁN FÖLDI.

ALIEN PROPERTY CUSTODIAN

PROCESS OF PREPARATION OF STEROL OXIDATION PRODUCTS CONTAINING TWO CARBONYL GROUPS

Hermann Bretschneider, Budapest, Hungary;
vested in the Alien Property Custodian

Application filed March 17, 1938

No Drawing. Application filed March 17, 1938

The oxidation of cholesterol, whose double bond is temporarily protected, was described by several authors already. This method of oxidation and the subsequent restoration of the double bond yielded cholestenone. In quite an analogous manner, sitosterol was oxydised to sitostenone. No record was found, however, showing, that diketones can be produced and separated from the raw oxydation mixture of such or similar sterols. I have now found that sterols or sterol derivatives containing at least one free hydroxyl groups whose carbon atom configuration between the carbon atoms 1-22, both inclusive, is identical with the corresponding carbon atom configurations of either cholesterol, or allo-cholesterol or epicholesterol, if treated—under temporary protection of the double bond—with oxidants able to split aliphatic chains, yield oxidation-mixtures which after restoring of the double bond, contain oxidation products having two carbonyl groups; these products can be obtained either in form of highly enriched extracts or in pure crystalline state.

As starting materials protected temporarily in the double bond the dibromo-derivatives of sterols, e. g. in case of cholesterol dibromo-cholesterol may be used. As oxidants permanganates, such as potassium permanganate, or chromic acid or chromates can be employed. It is of advantage if the oxidation is carried out in presence of mineral acids as, if so, the temperature can be kept lower than in the absence of those.

The valuable products of the present process are obtained by removing the acid substances from the oxidized starting material, subsequent restoring of the double bond, followed by elimination of starting material oxidized only in position 3, that is to say, e. g. in case of dibromo-cholesterol of cholestenone. The remaining prepurified product contains hormonally active oxydation products, such as androstendione and corpus luteum hormone which can be enriched in extracts suitable for practical purposes and, furthermore, can also be isolated in crystalline form.

From the crude reaction product obtained by oxidation I remove first the acid substances re-establish then the double bond and remove then starting material oxidized only in position 3—e. g. in case of dibromo-cholesterol the cholestenone—by recrystallization from acetone, or in some other way, e. g. by distribution between water-miscible and water-immiscible solvents such as methyl alcohol and petrol ether, in which case the bulk of the cholestenone will pass into the

petrol ether layer. The product thus freed from the greater part of cholestenone is then subjected either directly or after removal of constituents less soluble in methyl alcohol to a chromatographical selection, e. g. in benzene solution using aluminum oxide as absorbent. The sterol oxidation products containing two carbonyl groups pass the aluminiumoxyde column unaffected and remain in the filtrate. Further enrichment was achieved by extracting the petrol ether solution of the residue of this filtrate with aqueous 90 per cent methyl alcohol, thus collecting the greater part of the oxidation products containing two carbonyl groups in the methyl alcohol layer.

In order to obtain the hormones in crystalline state, the benzene filtrate, which passed the aluminium oxide column is evaporated and the resulting residue is dissolved in petrol ether. This solution is subjected to a repeated chromatographical selection, preferably on aluminium oxide and—as the case might be—in the presence of a suitable dye as e. g. sudan-III, which acts as an indicator. In this case, however, the hormones are absorbed by and remain in the aluminium oxide column; the distribution of the products containing two carbonyl groups is marked by the indicator used. The top-layers of the column will contain androstendione practically free from corpus luteum hormone, while the lower layers will contain this hormone contaminated with androstendione. After separating the different layers of the column each layer containing the hormone and the hormone-mixture are extracted separately by ether, methyl alcohol or alcohol. Further purification can be effected by evaporating the ethereal or alcoholic solutions thus obtained, and by distribution of the respective residues between aqueous methyl alcohol and petrol ether, in course of which the water-content of the methyl alcohol is gradually increased, the two hormones are collected in the methyl alcohol layer.

These methods of distribution and of chromatographical selection, repeated several times if necessary, yield concentrates which contain the hormones practically free from each another; from these concentrates the hormones may be isolated—eventually after foregoing distillation in high vacuo—in pure crystalline form.

The products prepared from the top and from the lower layers of the chromatographical column may be freed from the indicator and subjected to a repeated chromatographical selection, eventually after foregoing purification by the distribution method mentioned above. This second chromato-

graphic selection is preferably performed with a benzene-petrol ether solution of the hormones and with aluminium oxide as adsorbent. The first batches of the solution passing the column contain corpus luteum hormone, whereas the later ones and the column itself render androstendione.

The fractions, obtained by the separation methods described further above, containing the compounds with two carbonyl groups, can also be brought into reaction with ketone-reagents, e. g. with semicarbazide. The ketone-derivatives thus obtained are subjected to fractionating crystallization, e. g. in case of semicarbazones to repeated recrystallization from alcohol, by which the mixture can be separated into several fractions enriched in compounds containing two carbonyl groups, these fractions being now more separated from each other. From these ketone-derivatives fractions the ketones are subsequently regenerated and, if necessary, distilled in high vacuô.

The above mentioned refining processes may be employed in other sequences; the single stages may be repeated or combined according to need, by which sterol oxidation products containing two carbonyl groups are obtained in form of enriched extracts or of pure crystalline state.

Side-fractions obtained in course of the refinement process not quite freed from sterol oxidation products containing two carbonyl groups may be collected and re-introduced into the next batch at a suitable stage of the purification process.

The details of the new processes are explained by the following examples:

Examples

1. One kg of cholesterol is dissolved in 14 kg of carbon-tetrachloride and brominated with 0.42 kg. of bromine dissolved in 1.5 kg. of carbon-tetrachloride (Solution "A").

In a mixture of 9 kgs of glacial acetic acid and of 1 kg. of water 2.57 kgs of chromic acid (chromium trioxide) are dissolved by heating (Solution "B").

Into a mixture of 8.46 kgs of carbon-tetrachloride, 19 kgs of glacial acetic acid and 3.53 kgs of concentrated sulphuric acid the solutions "A" and "B" are introduced, under energetic cooling and stirring, in such a way that the velocity of addition of both solutions should be the same; the volumina of the added solutions should be about 2 litres per hour and the rise of temperature should not exceed 10°C. After further stirring for another half an hour 1.4 kg of methyl alcohol is added in small portions and stirring is continued for a period of 2 hours. Subsequently 3.3 kgs of sodium acetate are introduced and stirred for 30 minutes. The solution which should show a neutral reaction against congo-paper, an acid reaction against litmus and a positive test with potassium iodide starch paper, is evaporated in vacuum at a temperature not exceeding 65°C. The resulting residue is redissolved in warm water and extracted several times with benzene. The united benzene-extracts are evaporated and washed subsequently with water, 10 per cent sodium hydroxide solution, diluted sulphuric acid and again with water until neutral reaction, dried over anhydrous sodium sulphate and evaporated in vacuô in the presence of a little zinc dust.

The remaining neutral bromide-product is dissolved in glacial acetic acid of the same weight and de-brominated under cooling and stirring by zinc dust of the same weight. The addition of

zinc dust depends on the time and on the cooling. It lasts about one hour and a half, during which the temperature of the mixture is kept at about 30°C and is allowed to rise to 35-40°C only when the reaction is nearly over. When the total amount of zinc dust is introduced, glacial acetic acid is added, the weight of which being the same as that used originally for dissolving the bromine-product, and stirring is continued for 20 minutes at 50°C. Then the mixture is cooled to 15-20°C, diluted with benzene under continued stirring and the resulting solution washed—after removal of the solid parts—with water diluted sodium hydroxide solution and again with water until the reaction becomes neutral. The benzene solution, after being dried over anhydrous sodium sulphate, is evaporated in vacuô and the resulting residue is dried at a pressure of 1 mm at 70°C.

In order to remove cholestenone, the residue is recrystallized from acetone of the same weight. The mother-liquor of the cholestenone crystals is freed from the solvent in vacuô and yields 200 grams of a residue which is subsequently redissolved in methyl alcohol of the same weight and chilled to -12°C under stirring. Two layers are formed. The upper layer is removed by decantation and the one below is extracted 3-4 times with methyl alcohol. The methyl alcoholic solutions are united and evaporated in vacuô until constance of weight. The residue weighs about 100 grams and exhibits strong activity in the corpus luteum test.

This said residue (X) can be further purified e. g. by chromatographical analysis. One-hundred grms of this products are dissolved in benzene and the solution made to pass a tube filled with 1 kgs of aluminium oxide prepared sec. Brockmann and the tube is washed out subsequently with benzene. The resulting benzene filtrate is evaporated, the residue thus obtained redissolved in petrol ether and re-chromatographed on aluminium oxide. This time the diketones remain in the column absorbed. If a small amount of sudan-III is added to the original petrol ether solution, the division of the column, after the chromatogram has been developed, provides no difficulty. The content of the tube, beginning from the top down to the bottom of a well marked dark red colour ring, is taken out and subjected to further treatment. In the upper third part of the column is androstendione present, practically free from corpus luteum hormone, whereas in the lower two third parts corpus luteum hormone is found contaminated with androstendione. These parts of the column are separated from each other, and from each the adsorbed products are eluted by several extractions with boiling methyl alcohol (ethyl alcohol or ether). The elutes are evaporated to a small volumen, the dye-stuff is removed by active charcoal and cholestandione is precipitated by chilling and, if necessary, by seeding. The mother-liquor thus obtained from the elute of the upper part of the column is evaporated; it is rich in androstendion. The mother-liquor similarly obtained from the elute of the lower two thirds of the column is evaporated; it contains androstendion and corpus luteum hormone in a concentrated state.

2. One kgr of cholesterol, dissolved in 27 kgrs of carbon-tetrachloride, is brominated with 0.42 kgr of bromine, dissolved in 1.6 gr of carbon-tetrachloride. The resulting solution of dibromocholesterol is energetically stirred or shaken with 41 litres of a 5 per cent aqueous solution of potas-

sium permanganate and with a mixture of 1.05 kgr of concentrated sulphuric acid and of 0.6 kgr of water, at 25–30°. When the aqueous layer becomes decolorized, 2.1 kgr of finely powdered potassium permanganate is added in small portions and the stirring or shaking is maintained until the aqueous layer becomes again decolorized. At this point 2.5 kgrs of sodium bisulphite are introduced in order to remove manganese dioxide, after which the carbon-tetrachloride layer is separated and the aqueous layer is repeatedly extracted with carbon-tetrachloride. The united carbon-tetrachloride solutions are washed with sodium hydroxide solution and subsequently with water and evaporated in vacuo in the presence of a little calcium carbonate. The resulting residue is debrominated according to the description given in Example 1.

In order to remove cholestenone the debrominated product is dissolved in petrol ether of about 5 times its weight and extracted 6–7 times with 90 per cent methyl alcohol of the same weight. Cholestenone is collected in the petrol ether layer.

The aqueous methyl alcohol solutions are evaporated until a resinic substance precipitates, which together with the solution is extracted 3 times with benzene; the benzene solutions are washed with water in order to remove the last traces of methyl alcohol. The benzene solutions yield on evaporation about 100 grms of a residue of high corpus luteum hormone activity which can still be increased by way of chromatography. This is realized by redissolving the residue in benzene of 5 times of its weight and made to pass a tube filled with aluminium oxide of 15 times of its weight and washing the column with benzene. The benzenic solution yields on evaporation about 60 grms of a straw yellow resin, which is redissolved in a mixture of 300 cc. of petrol ether and of 90 cc. of methyl alcohol and mixed under shaking with 10 cc. of water, in order to effect further enrichment. The petrol ether layer separates and is extracted in subsequence 4 times aqueous 90 per cent methyl alcohol using 100 cc. on each occasion. The methyl alcoholic fractions are united and evaporated. The resulting residue is taken up in benzene and washed with water in order to remove last traces of methyl alcohol. On evaporation 10 grms of a straw coloured resin is obtained which in the physiological test exhibits a very high corpus luteum hormone activity. This product is an excellent starting material for isolation of the diketones in crystallized state.

3. The procedure is essentially the same as described in Example 1 as far as obtaining the products readily soluble in methyl alcohol. Further purification was effected in the following way:

One-hundred grms of the product (X) readily soluble in methyl alcohol were dissolved in a mixture of 500 cc. of petrol ether and of 90 cc. of methyl alcohol and distributed between these two solvents by addition of 10 cc. of water under thorough shaking. The petrol ether layer thus separating was extracted 6 times with 90 per cent methyl alcohol using 100 cc. of the latter each times. The methyl alcohol extracts were united and evaporated and yield 60 grms of a straw coloured resin which was subjected in subsequence to chromatographical selection.

The benzene solution of this resin was made to pass a tube filled with Brockmann's aluminium oxide and the column was washed with benzene. The filtrate was concentrated to a smaller

volumen and again chromatographed in a tube filled with aluminium oxide. Thus the benzene filtrate yields 20 grms of a residue when evaporated.

5 This residue was redissolved in 100 cc. of petrol ether, 0.25 grm. of sudan-III was added, after which it was made to pass a tube filled with 400 grms. of Brockmann's aluminium oxide the column being washed subsequently with petrol ether. 10 After the chromatogram is fully developed the column is divided according to the description given in Example 1. The lower two third layers were extracted with methyl alcohol. The extract yields on evaporation 6.5 grms. of a residue showing strong corpus luteum hormone activity in the physiological test. The layer of the upper third part of the column contain a product which exhibits strong activity in the vesicular test.

20 4. The product obtained according to the process described in Example 1 was subjected to a further selection in the following way:

Eighteen grms. of the product obtained from the lower two third parts of the petrol ether chromatogram of Example 1 were dissolved in 800 cc. of absolute alcohol and heated for two hours on a steam-bath with semicarbazide acetate, prepared from 21.3 grms. of semicarbazide hydrochloride and 26 grms. of sodium acetate. 30 During this procedure the mixture was concentrated to about 400 cc. After allowed to stand for 24 hours in the ice-chest, the crystals of crude semicarbazone were filtered by suction triturated with hot water and, subsequently, after drying, 35 with ether. Nine grms. of a product were obtained, decomposing at 215–219° C.

From this semicarbazone 7.4 grms. were recrystallized in 300 cc. of boiling alcohol, yielding 4.7 grms. of a substance which decomposes at 225° C. This product, if recrystallized from 1000 cc. of boiling alcohol and allowed to stand at 0° C. for a longer period, yields a product which weighs 1.5 grms. and decomposes above 300° C. The mother-liquor of these crystals contain another product which decomposes at 221° C.

The substance of the decomposition-point of above 300° C. was heated with 40 cc. of 96 per cent alcohol and 5 cc. of pyruvic acid for 2 hours, in course of which a clear solution is obtained. 50 This was poured into diluted alkali and extracted with ether. The ethereal extract was washed subsequently 3 times with sodium hydroxide solution, with diluted sulphuric acid and, finally, with water until neutral reaction. Evaporation of the ether gave 1.3 grm. of a substance which was distilled at a mercury pressure of 0.001 millimetre from an air-bath of 165–170° C. temperature. The distillate, which was recrystallized from a mixture of ether and petrol ether, is corpus luteum hormone.

60 The semicarbazone-fraction of the decomposition-point 221° C., obtained as mentioned above by evaporation of the alcoholic mother-liquor, yield on fission of the semicarbazone and on subsequent distillation in high vacuo crystalline androstendione.

5. The product obtained by the process described in Example 3 from the lower two third of the chromatogram can be re-purified in the 70 following way:

From this substance 6.5 grms. were dissolved in a mixture of 60 cc. of methyl alcohol and of 60 cc. of petrol ether and in small portions and under shaking 6.65 cc. of water were added. To the methyl alcohol layer thus separating 60 cc.

of petrol ether and, while shaking carefully, 8.35 cc. of water were added. The methyl alcohol layer obtained in this way was mixed again with 60 cc. of petrol ether and with 10.75 cc. of water, shaken thoroughly and then the petrol ether layer was removed. The methyl alcohol solution yields 2.02 grms. of a substance possessing a specific rotation of $(\alpha)_D + 109^{\circ}$ dissolved in absolute alcohol (Fraction "A").

The united petrol ether solutions yield 4.63 grms. of dry residue which were dissolved in a mixture of 100 cc. of petrol ether and of 90 cc. of methyl alcohol and distributed by addition of 10 cc. of water while shaking. The separating methyl alcohol layer was mixed with 100 cc. of petrol ether and afterwards 12.5 cc. of water were added in portions. The methyl alcohol layer again separates and was mixed again with 100 cc. of petrol ether and with 16 cc. of water this latter being added in small portions under shaking. The methyl alcohol contains a residue possessing the specific rotation of $(\alpha)_D + 104^{\circ}$ (Fraction "B").

The re-united petrol ether solutions obtained while preparing fraction "B" contain 3.98 grms. of a product which was subjected to the like treatment described above. The resulting methyl alcoholic solutions render 0.69 gm. of a substance of the specific rotation of $(\alpha)_D + 81.2^{\circ}$ (Fraction "C").

The fractions "A", "B" and "C" are united (3.38 grms.) and re-dissolved in a mixture of 10 cc. of benzene and of 30 cc. of petrol ether and the solution is made to pass a tube filled with 60 grms. of Brockmann's aluminium oxide that was previously soaked with benzene and petrol ether in the ratio 1:3. The chromatogram was developed by washing with the same solvent-mixture and the dry residue respectively the concentration of the passing solution was continually controlled. The concentration increases at the beginning, after which it falls rapidly and later decreases very slowly. From the passed solution nine fractions were taken, 15 cc. each, and evaporated.

The first fraction after being evaporated shows no tendency of crystallization; the residue of the second and the third fractions crystallize from an ether-petrol ether mixture and yield corpus luteum hormone. The fourth fraction still contains corpus luteum hormone but also androstendione. The fifth to ninth fractions render crystalline androstendione. However, the bulk of the androstendione remains absorbed in the column and is to be eluted with ether and recrystallized from the same solvent.

The last elutions with ether contain also a by-product, melting at 217°C .

6. The product obtained according to the process described in Example 3 from the lower two third parts of the chromatogram can be purified in the following way:

From this substance 6.5 grms are dissolved in 180 cc. of alcohol and boiled for 2 hours with semi-carbazide acetate that was prepared from 7.7 grms of semicarbazide hydrochloride and 9.5 grms of sodium acetate, meanwhile concentrated to 130 cc. and allowed to crystallize over night. The crystals are filtered by suction, extracted with boiling water, then dried and finally washed with ether. In this way 5.6 grms of a semicarbazone are obtained of the decomposition-point of $275-280^{\circ}\text{C}$. This semicarbazone of 5.6 grms are suspended in 75 cc. of alcohol, 10 cc. of pyruvic acid are added and the mixture is boiled for three hours and a half, in course of which clear solution is obtained. In subsequence the mixture was poured into 200 cc. of a 10 per cent solution of potassium carbonate, diluted with water and extracted with ether. The ethereal extracts are washed with diluted solutions of potassium carbonate, with diluted sulphuric acid and with water until neutral reaction was reached and finally evaporated. The product thus obtained weighs 3.4 grms, showing a specific rotation of $(\alpha)_D + 98^{\circ}$.

In a mixture of benzene and petrol ether of the ratio 1:3 3.4 grms of this product are dissolved and chromatographed in a tube containing 75 grms of Brockmann's aluminium oxide. The concentration of the solution passing the column increases at the beginning but decreases considerably later on. The filtrate renders 1.02 gm of a residue which gives rise to a substance of the melting-point $126-127^{\circ}$ if recrystallized from a mixture of ether and petrol ether. The mother-liquor of these crystals and the ethereal elutions of the column give 2.14 grms of a product which yields, on repeated chromatographical analysis as used in example 5 for purifying the united fractions A, B and C and recrystallization, corpus luteum hormone and androstendione.

The experimental conditions of the examples given above may be varied in several instances. For instance, instead of cholesterol also other sterols e. g. allocholesterol, epicholesterol, sitosterol and the likes may be used as a starting material.

HERMANN BRETSCHNEIDER.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF MALE SEXUAL HORMONE

Ernst Laqueur, Karoly Gyula David, Elizabeth Dingemanse, and Janos Freud, Amsterdam, Holland; vested in the Alien Property Custodian

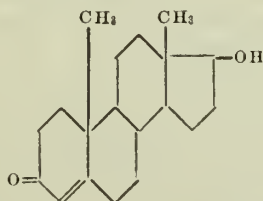
No Drawing. Application filed April 14, 1938

This invention relates to a male sex hormone in a crystalline state, called testosterone, capable of affecting growth of the comb of capons and of certain reproductive organs of mammals.

It has particular reference to the pure crystalline product which can be obtained by a process in which organs containing testosterone are extracted and which extracts are purified, this being a division of application No. 122,324.

A process for the preparation of the crystalline substance shall now be described.

Organs containing testosterone, for instance testicles, are extracted with organic solvents being miscible with water. Preferably acetone is used in such a quantity that during the extraction a concentration of the acetone of 60% is maintained. Thereupon the organic solvent of the extract is removed, for instance by distillation and the remaining liquid is repeatedly extracted with a solvent immiscible with water, preferably benzene is used. A distribution of the extract between the two layers of a solvent mixture forming two phases may be inserted, for instance between 70% alcohol and petroleum ether. In case the solvent wherein the crude testosterone is dissolved is not indifferent to sulphuric acid it has to be replaced by such a solvent, for instance benzene. This solution is repeatedly extracted with 55%-75% sulphuric acid. The sulphuric acid layers are separated, diluted with water and extracted with an organic solvent. After evaporation of the solvent the residue is distilled in a high vacuum, whereby the fraction distilling between 110°-130° C is separated. This fraction is recrystallized from organic solvents, preferably hexane and acetone until a constant melting point of 154,5°C (corr) is reached. This material consists of needles having the formula $C_{19}H_{28}O_2$. It has a specific rotation $(\alpha)_D^{20} = +109^\circ$ (C=1 in abs. alcohol). Its maximum of absorption of ultraviolet light lies between 2.400 Å. Its structure is represented by the following formula



It forms an acetate having a melting point of 140-141°C (corr) and an oxime having a melting point of 222-223°C (corr). About 15% of this material contain 1 capon unit, i. e. the effect of 100% androsterone,

A method for the preparation of the new crystalline hormone, called testosterone, will now be described:

Example 1.—235 kgs testicles of bulls are extracted according to Gallagher and Koch (J. Biol. Chem. 84, 495, 1929) with alcohol, the alcohol is evaporated, the residuing solution is extracted with benzene, the benzene is evaporated and the residue extracted with acetone, the acetone solution is frozen, the precipitate is removed and after evaporation of the acetone the residue is distributed between a mixture of 70% alcohol and petroleum ether. From the alcohol layer which contains the main part of the testosterone, the solvent is evaporated, whereby 283 gs residue remain. The residue is dissolved in 3,6 Lts benzene and twice shaken with 600 ccm 60% sulphuric acid and once with 600 ccm 70% sulphuric acid. The separated sulphuric acid layers are united and poured into 3,6 Lts icewater and four times extracted with 800 ccm ether. The ether solution is washed with 100 ccm 10% KOH and thereupon with distilled water until it has become neutral. It is dried with some sodium sulfate. After evaporation of the ether 345 mgs (=1,47 mg per kg testicles) residue remain, forming a viscous yellow-brown oil. The estimation of the physiological activity of this fraction shows that it contains 1 capon unit per 50 %, that means that 30 capon units per kg testicles are obtained. This oil is submitted to a fractionating high vacuum distillation at a pressure less than 0,001 mm whereupon the fraction distilling between 110-130°C is three times boiled with 20 ccm hexane. The united hexane solutions are concentrated by evaporation to a third of their volumes and kept at about 0°C. After several hours a yellow-white granular material separates, which is filtered off, washed with cold hexane and recrystallized several times from diluted acetone until white prismatic needles [M.P. 154-154,5°C [corr]] are obtained. Per kilogramme testicles 10 capon units are gained as crystals (See page 3, 1. 13/14).

Example 2.—250 kgs testicles of bulls are extracted with 250 Lts of 98% acetone. The liquid is separated and the residue is extracted again, this time with 250 Lts of 60% acetone. From the united extracts the acetone is evaporated and the remaining solution is extracted with 100 Lts benzene. The benzene solution, which contains 280 gs of solid matter, is submitted to the process described in Example 1 beginning with the treatment with sulphuric acid.

ERNST LAQUEUR.
KAROLY GYULA DAVID.
ELIZABETH DINGEMANSE.
JANOS FREUD.

THE JOURNAL OF THE

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ALIEN PROPERTY CUSTODIAN

METHOD FOR THE PRODUCTION OF HIGHER MOLECULAR MERCAPTALS AND MERCAPTOLS

Erik Schirm, Dessau/Anhalt, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 4, 1938

It is known that mercaptans with oxo-compounds i. e. with aldehydes and ketones allow of being condensed, by means of hydrogen-halide, to mercaptals or mercaptols respectively. However, those condensation-products were hitherto made and reapplied in technical proportions but in exceptional cases.

Now it has been found that technically valuable higher molecular mercaptals and mercaptols respectively are obtainable for many purposes in condensing mercaptans with no less than 8 C atoms in the molecule and particularly those of the aliphatic series and eventually in the presence of diluents, with oxo-compounds viz. aldehydes, ketones and other compounds containing the carbonyl group or with the ethers ("acetals") or carboxylic acid esters of the oxo-compounds. It was surprising that, as stated within the limits of the present method, the condensation of the oxo-compounds with the higher molecular mercaptans takes an absolutely smooth course. The present procedure therefore constitutes a simple and productive method for the formation of very high molecular and multifarious compounds by the possibility of introducing two higher molecular hydrocarbon residues in a single operation being combined very fastly by means of sulfur atoms into the molecule of oxo-compounds of very different kinds. The thus obtained mercaptals or mercaptols respectively are—which is remarkable—perfectly fast to the reaction of acids and alkalis, apart a few exceptions depending on a peculiar structure of the initial stuffs.

As initial materials for the present invention we may consider any aliphatic mercaptans of a straight or of a ramified chain, further any cycloaliphatic, aromatic, fatty-aromatic, cycloaliphatic-aromatic and cycloaliphatic-fattyaromatic mercaptans and the like such as octyl-, dodecyl-, oleyl-, docosyl-mercaptan, as well as the 2-decahydronaphthyl-, 1-and 2-naphthyl-, 1-menaphthyl, tetrahydro-menaphthyl-mercaptan, the 9-mercaptomethyl-octohydroanthracene etc. The carbon chain of those mercaptans may also be interrupted one or several times by hetero-atoms or hetero-atom groups such as O,S,NR,CO, SO₂, CO.O, CO.NR, SO₂.NR(R=H or hydrocarbon residue).

For the oxo-compounds serving as second initial component we may, on principle, apply all wellknown oxo-compounds as far as the carbonyl groups contained therein—eventually also several times—are of a sufficient reactivity.

As single or manifold oxo-compounds applicable

for the present method there are to be mentioned: formaldehyde and acetaldehyde in their monomeric or polymeric forms, crotonic aldehyde, glyoxal, acetone, palmitone, stearone, mesityl-oxide, acetyl-acetone, cyclo-hexanone, acetophenone, stearo-phenone, benzaldehyde, benzophenone, cinnamic-aldehyde and the like, as well as their ethers and esters such as methylal, ethylal, acetal, ethylidene di-acetate etc. The oxo-compounds may also contain substituents such as nitro groups, further hydrophile groups such as hydroxyl groups, substituted or non-substituted amino groups, quarternary ammonium groups, ether-, carboxyl-, sulfonyl-, sulfonic acid groups and the like or such atoms or atom groups which allow of being easily converted into hydrophile atom groups such as halogen atoms, S, SH, —S.S—. Oxo-compounds of this kind are e. g. aldol, acetonyl-methyl alcohol, glucose, acetic acid ester, levulinic acid, benzoin, phenoxy-acetone, o-benzoyl-benzoic acid, p-tolyl-acetonyl-sulfone, benzaldehyde-m-sulfonic acid, mono- and dichloroacetal, amino-acetal, chloral, mono-chloroacetone, ω-chloro-acetophenone.

The mercaptals and mercaptoles respectively produced according to the present invention of the oxo-compounds and of the higher molecular mercaptans are of a wax-like character especially when the high-molecular cetyl-, octadecyl-, eicosyl, docosyl-, montanyl-mercaptans and the like are applied; in all industries where wax is worked up they will be used with good results.

Moreover the mercaptals and mercaptoles respectively are—either alone or after the introduction of hydrophile atom groups—most suitable as wetting-out-, dispersing-, lathering-, detergent-, dissolving-, softening agents and the like in the washing-means-, textile-, leather-, paper- and similar industries.

The nitro-substituted mercaptals and mercaptoles respectively are further apt e. g. as intermediate products for the manufacture of dyestuffs, means of combating pests and medicaments.

Example 1

1 weight-part of paraformaldehyde is suspended in a solution of 17 weight-parts of cetyl-mercaptan in 34 weight-parts of benzene; then, while stirring at room-temperature, we introduce hydrogen chloride-gas into the mixture until the suspended paraformaldehyde has disappeared and no free mercaptan being any longer detectable in the solution. The benzene is then dis-

tilled off under reduced pressure and thus the formaldehyde-dicetyl-mercaptan is obtained as residue in the form of a wax-like mass.

Example 2

11 weight-parts of mono-chloro-acetal and 21 of n-octyl-mercaptan are mixed, whereupon hydrogen chloride-gas is introduced until the reaction-component is completely converted. The thus obtained chloro-acetaldehyde-dioctyl-mercaptan, in oil-form, is now liberated from the hydrochloric acid by washing with water. The Cl atom present in this compound may be substituted by a SO_3H group, in which case we obtain a product of surface-active properties and soluble in water.

Example 3

Into a mixture of 2 weight-parts of dodecyl-mercaptan, 1 of glucose and 10 of alcohol, an amount of hydrogen chloride-gas is introduced while stirring and cooling until the mercaptan has completely disappeared. Then the reaction-mixture is poured into a large quantity of water, whereupon the amorphously separated reaction-product is filtered off and dried. The thus obtained glucose-didodecyl-mercaptan is applied as an excellent agent to emulsify in water or in aqueous solutions the most heterogeneous organic liquids, fats, oils and waxes otherwise insoluble in water.

Example 4

3 weight-parts of levulinic acid and 14 of octadecyl-mercaptan are dissolved in 45 weight-parts of ether. To this solution we admix half the volume of concentrated etheric hydrochloric acid; the mixture is then kept for one day at room temperature, whereupon the formed colourless crystal mass is sucked off. The resulting reaction product consisting of di-octadecyl-mercapto-valerianic acid is then re-crystallized from alcohol (melting point $72-74^\circ\text{C}$). This product allows of being applied as such or in the form of its esters or salts instead of wax.

Example 5

151 weight-parts of m-nitro-benzaldehyde and 573 of octadecyl-mercaptan are dissolved at room-temperature in 900 weight-parts of benzene. While cooling with cold water we introduce, at $20-25^\circ\text{C}$, an amount of hydrogen chloride-gas until the mixture is solidified to a paste-like mass. After a while we suck off and after drying we obtain appr. 70% of the total amount of the developed m-nitro-benzaldehyde-dioctadecyl-mercaptan in the form of a white powder (melting point $54-55^\circ\text{C}$). The residue is obtained by evaporating the benzene from the benzene-solution. The reaction-product is obtained in a nearly quantitative yield.

ERIK SCHIRM.

ALIEN PROPERTY CUSTODIAN

ANTI-FRICTION DEVICE

Rudolf Menger, Berlin, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed June 2, 1938

The heretofore known synthetic resin molding materials for anti-friction bearings contain as fillers fibrous materials, such as asbestos, paper, cotton, linen, etc. in random arrangement or also principally disposed in a direction to obtain from the molded bearing parts the highest possible mechanical strength.

Such bearings have initially uneven surfaces which do not give a low friction coefficient. The bearings in operation produce a relatively high frictional heat and accordingly are adapted only for small loads and low speeds. The surfaces of such bearings under the generated heat become more uneven, since the materials incorporated therein differ greatly in expansion. Furthermore the bearing surfaces made from the hereto known synthetic resin molding materials are for the most part porous and for that reason useless for heavy pressure bearings, since a durable continuous lubricating film cannot form as is the case with bearings having dense surfaces. Moreover, it follows from the porosity that the bearings, becoming compressed particularly under heavy variable loads, are soon after a short running period given an intolerably great play. Finally the porous bearing surfaces cause the sliding machine elements to become adherent to the bearing surfaces and therefore require a high starting effort.

Because of these experiences there has arisen the problem of providing molding materials that do not have the objections mentioned. The difficulty lies in fulfilling simultaneously five requirements placed upon bearings when in use, namely, a small friction coefficient, minimum porosity, great mechanical strength, high resistance to heat and a minimum deformation of a bearing under varying pressures. Further, in the selection of the ingredients for the molding materials care must be taken that neither the molds nor the sliding metal parts are attacked.

The hitherto known synthetic resin molding materials which, as has been stated before, contain fibrous fillers in random or orderly arrangement, fail in at least one of the described requirements. Likewise it is not possible to satisfy the demands placed on high quality bearings by using either mineral or organic materials in powder form as fillers.

It has now been found that it is possible to obtain synthetic resin molding materials by means of mixtures of pulverized inorganic and organic materials as fillers from which can be prepared bearings or molded bearing parts of

high quality and fulfilling all the prescribed requirements.

As inorganic ingredients found suitable are those of inferior or medium hardness, such as finely ground silicates exemplified by feldspar, soapstone, carbonates exemplified by marble and calcite besides oxides as bauxite, sulfates as heavy spar, fluorides as fluorite, and cryolite. Asbestos in fibrous or spun form can also be used. Precipitated inorganic materials do not meet the requirement of high mechanical strength, but it is the minerals in finely powdered or ground condition to which restriction is made by this requirement. As suitable organic ingredients are cotton flock, wood flour and preferably hardwood flour, and other finely ground cellulose materials.

A small addition, not over fifteen per cent by weight, of graphite to the molding mixture improves the properties of the bearings.

In the preparation of molding materials according to this invention with relation to the properties of the herein described bearings, it is found particularly advantageous to maintain certain quantity proportions between the inorganic and organic ingredients of the filler. These quantity proportions are such that in the filler mixture there are present from 35 to 85% of finely ground inorganic substances—as asbestos in fibrous or prespun form—and 15 to 65% of finely ground organic substances. The ratio of the organic to the inorganic ingredients can be modified within the limits set, depending upon whether the desired bearings are to possess greater resistance to heat or greater resistance to load.

Example 1

	Kilos
Marble dust -----	330
Woodflour -----	270
Phenol-novolak -----	300
Hexamethylenetetramine -----	50
Coloring and other usual additions -----	50
	1000

Example 2

	Kilos
Asbestos -----	420
Cotton flock -----	180
Phenol-novolak -----	300
Hexamethylenetetramine -----	50
Coloring material and other usual additions -----	50
	1000

Example 3

	Kilos
Heavy spar-----	360
Cellulose -----	150
Graphite -----	90
Phenol-novolak -----	300
Hexamethylenetetramine -----	50
Coloring material and other usual addi- tions -----	50
	1000

Molding materials are prepared from the mix-
tures in the usual manner by working on mixing
roll or kneading machines.

The heat of friction developed with a synthetic
resin bearing made from molding materials as
herein prepared approximates only about one-
eighth of that generated with metal bearings.

Measurements that have been made show that
bearings prepared from the described molding
materials support under the same conditions of
test from two to three times the load that white
metal bearings will endure. At a surface speed
of 8 meters per second without oil-reflux cooling,
bearings of white metal under test had a maxi-
mum load capacity of 60 kilos per square centi-
meter whereas bearings of the molding materials
here described showed no fatigue under a load of
150 kilos per square centimeter. Such results

have not heretofore been attained with synthetic
resin molding materials under like conditions;
their load capacities have amounted to only about
one-third of that of the new molding materials.

5 As the resinous bonding agent, the examples
specify the novolak or non-heat-hardening type
of phenol resin with which is included hexa-
methylenetetramine as a hardening agent. The
use of a novolak type is specified as it permits an
intimate mixing and fluxing of the binding agent
with the filler without setting up the resin.
Resins which are heat-hardening per se without
added hardening agent can be substituted in
whole or in part. Moreover it is possible to use
15 other heat-hardening types of resins, such as the
urea-formaldehyde type of resin. With such
heat-hardening resins care should be observed in
the mixing operation that the temperature is be-
low that at which substantial advancement of
the resin takes place so as to interfere with the
20 molding of the mixture.

The ground or powdered inorganic filler in-
cluded in the mixture is preferably of a substan-
tially water-insoluble nature characterized by in-
ferior hardness as stated and illustrated above.
25 In general these are included in major propor-
tion in the filler, as the examples bring out.

RUDOLF MENDER.

ALIEN PROPERTY CUSTODIAN

PROCESS OF SEPARATING OLEFINES FROM GASEOUS MIXTURES

Henri Martin Guinot, Niort, France; vested in the Alien Property Custodian

Application filed June 27, 1938

The necessity for utilising hydrocarbons of higher and higher octane number for supplying modern internal combustion engines has led to the practice of adding certain compounds such as the aliphatic alcohols and their ether oxides to the hydrocarbons customarily used. These substances are obtained in the most economical manner by starting from the olefines which are found either in the natural gases collected in certain countries or in the cracking gases provided by the pyrolysis of mineral oils or their heavy fractions of small value.

In any case, the olefines are generally obtained very much diluted in a large proportion of gases such as the corresponding saturated hydrocarbons, methane and hydrogen, and this complicates the problem of the ultimate transformation of these olefines into alcohols or ethers.

Furthermore, methods employing simple liquefaction followed by fractional distillation are of little use in separating the olefines because the boiling point of the olefines and the corresponding saturated hydrocarbons are mixed up in an inextricable fashion in the case of the C₄ and higher hydrocarbons, as the table below shows:—

		Boiling points at ordinary pressure
Ethylene	-----	-103° C.
Ethane	-----	-88°3 C.
Propene	-----	47°8 C.
Propane	-----	-44°5 C.
Butenes	Butene 1	-6°6 C.
	Butene 2	+0.3° C.
	Isobutene	+3° C.
	Isobutene	-6° C.
Butanes	Butane-n	-0.6° C.
	Isobutane	-10°2 C.

The present invention has for its object a simple and efficacious process for increasing the proportion of olefine in a gas mixture, or for separating the olefines from cracking or other gases.

Broadly speaking this object is attained by repeated extraction of olefines from a gaseous mixture by means of a solvent having a preferential solvent capacity for the olefines as compared with the diluent gases. This results in the gaseous mixture dissolved in the solvent containing a higher proportion of olefine than the gas in equilibrium with the solution. Hence by recovering the dissolved gases and treating them with solvent and repeating this solution and recovery as often as desired, olefines of any desired degree of purity may be obtained.

Thus according to the present invention a mix-

ture of olefines and diluent gases is treated with a solvent having a preferential solvent capacity for olefines, in a plurality of stages, each of which comprises a solution step, where the gases are dissolved, and a recovery step, where the dissolved gases are recovered from the solvent, the gases recovered from one stage being passed to the solution step of the succeeding stage.

Pressure above atmospheric is preferably used in the solution steps since it renders recovery of the gases easier and also increases the total amount of gas dissolved in a given amount of solvent. On the other hand, the difference between the respective solubilities of the olefines and the saturated hydrocarbons increases with temperature, so that, within certain limits, it is well not to carry out the separation at too low a temperature.

As solvent, there can be used pure water or water to which has been added a certain quantity of a liquid which has the property of increasing the solubility of all the gases forming the mixture, without however diminishing the difference between the solubility coefficients of the olefines on one hand and the diluent gases on the other hand.

It has already been proposed, for the separation of olefines from mixtures containing these substances, to use aqueous solutions of certain salts such as cuprous chloride, which are capable of exerting a chemical action on the olefines by attacking the double bond, to give unstable derivatives capable of being ultimately decomposed by heat to liberate the olefine. Contrary to this known method, the present invention does not bring any chemical reaction into play and only uses the phenomena of solution.

The following example, for the practical carrying out of which there can be used the installation diagrammatically shown on the accompanying drawing, will make the operation of the invention easily understood.

It will be supposed that it is desired to separate propylene from a fraction of cracking gas made up of:—

	Volumes
Propylene	20
Propane	80

and that the solvent used is pure water.

At the temperature of 20° C. and at atmospheric pressure, a litre of water can dissolve respectively 0.165 litre of propylene and 0.037 litre of propane.

To the base of a washing tower 1 provided with Raschig rings, there is admitted at a² through a

pipe a^1 , the gas to be treated, which is fed by a compressor 7 at a pressure of 6 kg/cm² for example. To the top of the tower the washing water under pressure, to the extent of about 101 m³ for each 100 m³ of gas (reckoned at atmospheric pressure) to be washed, is supplied at b^2 through a pipe b^1 with the help of a pump b .

The height of the washing tower is sufficient for propane practically free of propylene to escape from the top. 62.27 m³ of propane for each 100 m³ of gas treated escape from the tower. At the base of the tower there is obtained water containing in solution such a proportion of the two gases propane and propylene that it is substantially in equilibrium with the mixture treated.

This water is sent through a pipe c , through a valve c^1 , into a gas recovery tower 4, where there obtains a slight vacuum produced by a pump c and where, flowing over the baffles $4'$, the water completely gives up the gas which it held in solution: this gas is found to have a volume of 37.73 m³ at ordinary pressure and to have its proportion of propylene increased to 53% by volume. It is again compressed by the pump 3 and sent under a pressure of 6 kg/cm² to a tower 2, washed with 38 m³ of water for each 100 m³ (at atmospheric pressure) of gas initially treated.

There is thus separated, at the top of the tower 2, 13.81 m³ (at atmospheric pressure) of substantially pure propane which is sent to join the propane previously separated in the tower 1 and withdrawn from this latter. At the base of the tower 2, there is obtained a saturated aqueous solution in equilibrium with gas containing 55% of propylene. It is sent through a pipe d and through a valve d^1 into a gas recovery tower 5 where it gives up 23.92 m³ (at atmospheric pressure) of gas containing 83.5% of propylene by volume.

This gas is again taken by a compressor 9 and treated in a tower 3 associated with a gas recovery tower 6 like the towers 1 and 2 and which, in this recovery tower, will give propylene of 96.5% purity and a volume of 20.72 m³ at atmospheric pressure.

If it is desired to obtain greater purity, the gas could be subjected to other successive treatments so as to achieve the result sought.

In order to reduce as much as possible the costs of pumping inherent in the transference of large quantities of water under pressure, there can be added to the water, as has been stated above, a certain proportion of a carefully selected solvent so as to increase the solubility of the gases to be treated, without thereby substantially reducing the difference between the respective solubilities of the olefines and the corresponding saturated hydrocarbon.

It has already been proposed to employ the customary solvents such as the alcohols, the ether oxides and the esters, which are excellent solvents for the olefines, for the separation of olefines, but these liquids dissolve saturated hydrocarbons practically as well as they dissolve the olefines themselves, so that they cannot be used even in aqueous solutions for the separation in question, since the difference between the solubility coefficients of the gases to be separated, which difference alone permits efficacious separation, is then much less as will be seen clearly from the following figures which relate to the propane-propylene mixture at a temperature of 20° C. and at ordinary pressure:

—solubility of propylene in pure water: 0.165 litre/litre H₂O
—solubility of propane in pure water: 0.037 litre/litre H₂O.

5 With pure ethyl alcohol the solubilities of propylene and propane under the same conditions are respectively 8.9 1. 6.3 1.

10 It will thus be seen that the solubility of the mixture of the two gases considered is considerably augmented by the employment of alcohol. On the contrary, the ratio of the solubilities which is 4.45 in the case of pure water, is not more than 1.4 in the case of alcohol, which makes any practical separation impossible.

15 In the same way with normal propanol, the solubilities of propylene and propane are respectively 10.8 1. and 7.7 1. per litre propanol, which again gives a solubility ratio of 1.4.

20 This characteristic effect of ordinary solvents persists even in aqueous solutions. Thus with an aqueous solution of normal propanol at 20%, the solubility figures are 0.200 1./litre solution for propylene and 0.068 1./litre solution for propane. The improvement in solubility in comparison with pure water is therefore relatively small; the ratio of the solubilities however is reduced by the presence of 20% of propanol to 2.95 against 4.45 in the case of pure water. The employment of these solvents is therefore of no advantage.

30 A liquid such as carbitol (hydroxy-ethoxy-ethyl-ether) can, however, be used according to the present invention, since the mixtures of this substance with water comply with the desired conditions regarding the difference between the respective solubilities of the olefines and the diluent gases; thus for propane-propylene mixtures the following figures are found:

solubility of propylene in a solution of
40 50% of carbitol ----- 0.41 1./litre solution
solubility of propane in a solution of
50% of carbitol ----- 0.095 1./litre solution

45 It will be seen immediately that the difference between the respective coefficients of propane and propylene remains excellent (4.31 instead of 4.45 for pure water) which is essential, whereas the solubility of the whole has however increased in a substantial degree.

50 It is within the scope of the invention to utilize solvents of different composition in the various stages of the apparatus described.

55 The filled towers can be replaced by arrangements tending to the production of the same result, for example, by columns having plates or devices having means for agitation. The power used for compression can be recovered by utilizing in an appropriate manner the release of gases leaving the washing towers, for example to operate turbines or other similar devices.

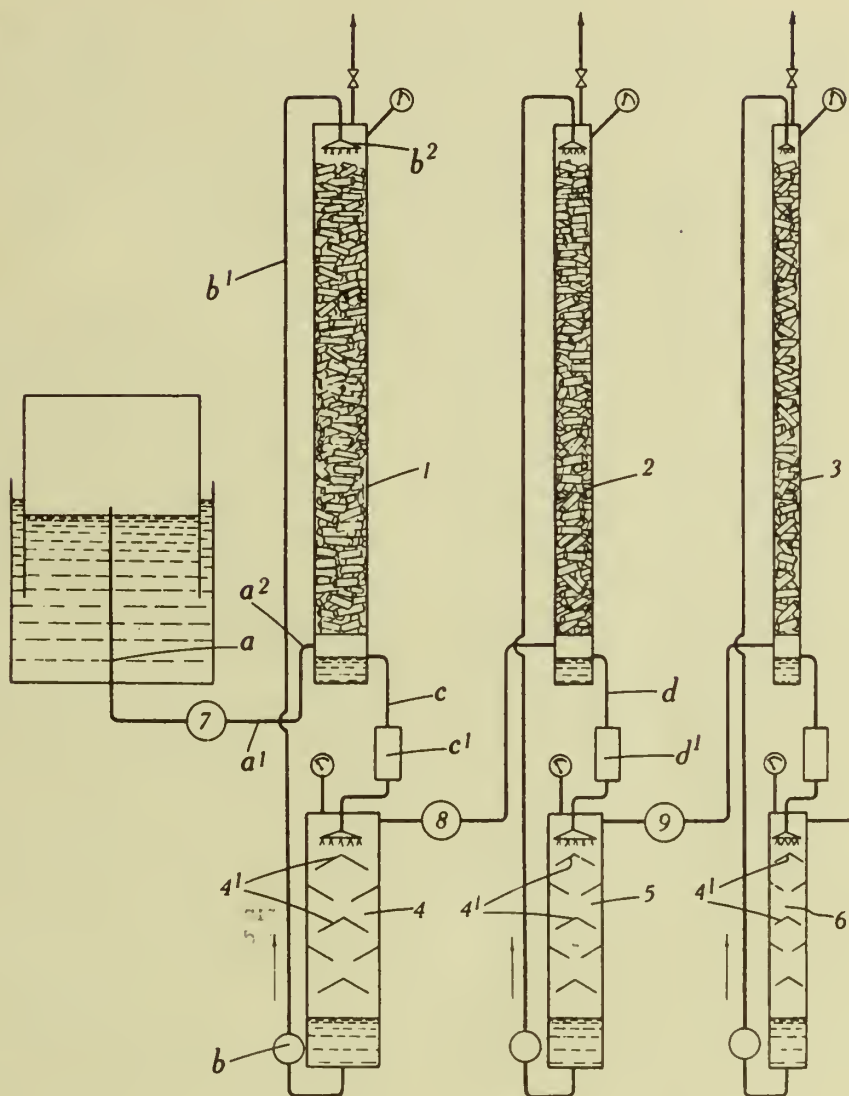
60 Finally, it is within the scope of the invention to make various modifications to the apparatus described and shown while maintaining the principle of separation explained above. In particular, it is sometimes advantageous to reduce the height of the washing towers 2, 3 etc. so as to obtain at the head, not practically pure saturated hydrocarbon, but a mixture of saturated hydrocarbon and olefines, this mixture being immediately returned, without preliminary release, to a suitable place in the tower 1, the diameter of which can be consequently augmented.

HENRI MARTIN GUINOT.

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H. M. GUINOT
PROCESS OF SEPARATING OLEFINES
FROM GASEOUS MIXTURES
Filed June 27, 1938

Serial No.
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Henri M. Guinot^{INVENTOR}
BY
J. Guinot
ATTORNEY

ALIEN PROPERTY CUSTODIAN

POLYISOBUTYLENE MIXTURE FOR ELECTRIC INSULATING PURPOSES

Hans Müller, Berlin-Wilmersdorf, and Hans Wassmansdorff, Falkensee, Kreis Ost-Haveland, Germany; vested in the Alien Property Custodian

No Drawing. Application filed June 29, 1938

This invention relates to a polyisobutylene mixture, particularly for electric insulating purposes.

The artificial substances manufactured from polyisobutylene are characterized by good electrical properties; however, particularly by a great impermeability to water. This artificial substance is, however, so elastic as not to be capable of being treated without admixtures in the usual manner on the calender or in the spraying machine. Endeavors have, therefore, already been made to facilitate the treatment of the polyisobutylene by admixtures. Thus, for instance, wax or montan resins have been proposed as softening means. However, by such admixtures the stability of form of the product, particularly in the case of high temperatures is so materially diminished that these mixtures cannot be employed for many purposes, particularly for electric insulating purposes. On the other hand inorganic filling materials decrease the impermeability of the polyisobutylene to water and the constancy of the electric values to a very considerable extent so that they are also not so suitable as to attain an electrically high-graded stable polyisobutylene mixture impermeable to water, but a polyisobutylene mixture capable of being properly machined.

According to the invention these drawbacks are removed by a polyisobutylene mixture which contains as a filling material cumarone resin or polystyrene or similar aromatic resin-like hydrocarbons having a dropping point above 100°, preferably above 125°. Small amounts of divinyl benzol preferably about 1% are added during the

polymerization to the polystyrene employed as a filling material, whereby the good properties of the mixture may be improved to a further extent.

A particularly fine distribution of the filling materials in the polyisobutylene may be obtained in the manner that the mechanically stirred mixture is heated to relatively high temperatures, for instance, to 120° centigrade or that the mixture is produced at this temperature and is thereafter cooled down again. The cooled mass is then rolled in the usual manner at lower temperatures, preferably below 50° centigrade in the case of cumarone resin mixtures and below 70° in the case of polystyrene mixtures. The mixing proportion between polyisobutylene and the filling material is preferably chosen within the limits between 2:1 and 2:3.

By the mixture according to the invention easily machineable and electrically high-graded products may be obtained whose shape is only impaired to a slight extent at high temperatures and which may be therefore suitably employed in manufacturing the insulation of electric conductors and cables.

The mixture is also particularly suitable for insertion as a layer impermeable to water in cable insulations or cable sheaths having a considerable permeability to water consisting, for instance, of acrylic acid ester, ethyl cellulose, impregnated fibrous material etc. or of a layer of different substances.

HANS MÜLLER.
HANS WASSMANSDORFF.

ALIEN PROPERTY CUSTODIAN

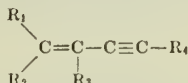
SYNTHETIC RUBBER

Alessandro Maximoff, Milano, Italy; vested in the
Alien Property Custodian

No Drawing. Application filed July 16, 1938

This invention relates to a process for the manufacture of valuable rubber like masses.

In accordance with the present invention butadiene or its homologues are polymerised with hydrocarbons of the general formula:



wherein R_1 , R_2 , R_3 , R_4 are either hydrogen-atoms or any organic hydrocarbon radicals.

Such hydrocarbons may be polymerised in admixture with butadiene and/or its homologues thus yielding polymers of better mechanical properties than pure butadiene polymerizates.

The polymerization of a mixture of the said hydrocarbons with butadiene may be effected according to any of the following methods:

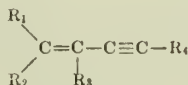
1. Polymerization by the action of the usual catalysts, without solvents.

2. Polymerization in the solution state, using as solvents ketones, alcohols or hydrocarbons which latter must be stable to polymerization, such as benzene or gasoline.

3. Polymerization in the emulsified state.

From a technological stand point this latter is the best method.

Hydrocarbons corresponding to the general formula



may be added to butadiene in any desired proportion, but the best results were obtained within a range between 20 and 150% by weight of butadiene or its homologues.

The following examples will further illustrate the nature of this invention.

Example 1

To 160 parts of water there are added:

40 parts of a 10% ammonia solution

2 parts of a 30% hydrogen peroxide solution

A second solution, containing:

100 parts of butadiene

35 parts of vinylacetylene

10 parts of oleic acid

is introduced under suitable pressure into the first solution thus forming a dispersion or artificial latex, and the mixture is polymerized at

50-60° C. for about 72 hours, under continuous shaking.

The dispersion is then cooled to normal temperature, and the non-polymerized hydrocarbons are distilled off: the remaining latex is coagulated by addition of acetic acid, and the rubber coagulum is washed with water in a rubber mill and finally an amount of 2-3% of an antioxidizing agent such as phenyl-beta-naphtylamine is incorporated therein.

Example 2

8 parts of acetic acid

1 part of trichloroacetic acid and

1.5 parts of benzoyl peroxide are dissolved into 200 parts of water.

A second solution, prepared by adding to:

100 parts of butadiene

50 parts of monophenyl - vinyl - acetylene and

10 parts of saponin

is introduced under suitable pressure into the first solution, thus forming a dispersion or artificial latex, and the mixture is polymerized at 40° C. for 3 to 5 days under continuous shaking.

The resilient polymerization product is obtained by coagulation of the emulsion with acetone or with a sodium chloride solution. The coagulum is washed with water and a preserving agent is incorporated therein.

Example 3

To 200 parts of water there are added:

5 parts of casein

8 parts of the sodium salt of the butyl-naphthalene-sulphonic acid

3 parts of a 30% solution of hydrogen peroxide

A second solution prepared by adding to:

100 parts of butadiene,

60 parts of monomethyl vinyl acetylene

is introduced into the first solution, and the mixture is polymerised as in the preceding examples.

The above examples have been reported to illustrate how the present invention is to be carried out in practice, but the invention is not restricted to these examples, as other acetylene homologues as well as other emulsifying substances or other catalysts may be usefully employed.

ALESSANDRO MAXIMOFF.

ALIEN PROPERTY CUSTODIAN

SYNTHETIC RUBBER

Alessandro Maximoff, Milano, Italy; vested in the
Alien Property Custodian

No Drawing. Application filed July 19, 1938

This invention relates to a process for the manufacture of valuable rubber like masses.

In accordance with the present invention, butadiene, or its homologues, or their mixtures are polymerised with aliphatic or alicyclic hydrocarbons of the general formula:



wherein x is at least equal to 4, and in which at least one pair of conjugated ethylenic double bonds is present.

Hydrocarbons corresponding to the above general formula are, for example: myrcene, α -phellandrene, β -phellandrene, α -terpinene, 1-methyl-4 isopropenyltetrahydrobenzene, 1-methyl-4-isopropenyl 1-3 di-hydrobenzene etc.

Such hydrocarbons may be polymerized with butadiene or its homologues thus yielding mixed polymers or better mechanical properties than pure butadiene polymerizates.

The polymerization of a mixture of the above hydrocarbons with butadiene may be carried out according to any of the following methods:

1. Polymerization by the action of the usual catalysts and in the absence of solvents.

2. Polymerization in the solution state, using as solvents ketones, alcohols, or hydrocarbons which latter are stable to polymerization such as benzene or gasoline.

3. Polymerization in the emulsified state.

From a technological standpoint this latter is the simplest and best method. The hydrocarbons in question may be added to butadiene and or its homologues in any desired proportion, but the best results were obtained within a range between 20 and 150% by weight of butadiene or its homologues.

The following examples will further illustrate the nature of this invention.

Example I

	Parts
Butadiene	100
Myrcene	60
Oleic acid	12
A 2% ammonia solution	170
A 3% hydrogen peroxyde solution	30

The mixture of the above substances which forms a dispersion or artificial latex, is polymerised at 50–60° C for 4 days, while subjected to continuous stirring.

The mixture is then cooled and the rubber coagulated by means of acetic acid.

Example 2

	Parts
Butadiene	70
Isoprene	30
Methyl 1-isopropenyl 4-tetrahydrobenzene 1-3	35
A 7% solution of diethyl amino ethyleoil amide hydrochloride	150
Acetic acid	2
Thichloroacetic acid	3

The mixture of the above substances which constitutes a dispersion or artificial latex is polymerised at 50° C for 2–3 days while continuously stirred. The product obtained, which is similar to latex is treated for example with acetone or with a saturated solution of sodium chloride, and the coagulated rubber-like mass is separated, washed and dried.

The above examples have been reported to illustrate how the said invention may be carried out in practice, but the invention is not restricted to these examples. For instance other hydrocarbons corresponding to the general formula C_nH_{2n-x} as well as other emulsifying substances or other catalysts than those disclosed above may be employed.

Similarly the range of times and temperatures of the polymerization process may be varied, within very wide limites.

ALESSANDRO MAXIMOFF.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR CONVERTING TRICHLOR ETHYLENE

Walter Bauer, Darmstadt, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed July 25, 1938

The invention relates to the production of technically valuable chlorinated hydrocarbons from trichlor ethylene.

It has been described that trichlor ethylene can be polymerized by the action of aluminum chloride to yield oils or substances of resin-like character. Furthermore it has been proposed to polymerize trichlor ethylene in the presence of organic vinyl esters to yield joint polymers with said esters. It is also known to use trichlor ethylene as a solvent for acrylic acid or its derivatives, when polymerizing the said compounds with the aid of oxygen or substances evolving oxygen.

It has been stated that the action of oxygen on trichlor ethylene even together with the action of ultra violet rays yields only dichlor acetyl chloride and no polymeric compounds.

It was surprising therefore that according to the present invention trichlor ethylene can be polymerized per se by treating with a peroxide. The polymeric compounds which are obtained by the new process are however quite different from the oils or resin-like substances obtained by the action of aluminum chloride on trichlor ethylene. The reaction products obtained from trichlor ethylene treated with peroxides are substantially dimeric and trimeric, liquid products besides some higher polymeric substances.

Suitable peroxides to be used according to the invention are inorganic peroxides and organic peroxides, e. g., benzoyl peroxide or tetrahydronaphthalene peroxide.

Trichlor ethylene can be treated with peroxides in admixture with symmetrical dichlor ethylene. In this case polymeric trichlor ethylenes, polymeric symmetrical dichlor ethylenes and addition products which contain trichlor ethylene and symmetrical dichlor ethylene are obtained.

Besides peroxides, heat or pressure alone or combined together may be employed to assist the polymerization.

The new process is especially advantageous since the splitting off of hydrogen chloride (effected by aluminum chloride in any case) is avoided practically completely when temperatures lower than about 150° C. are used. Above 150° C. decomposition (especially splitting off of hydrogen chloride) occurs and the reaction vessels may be affected.

The reaction may conveniently be carried out by boiling at atmospheric pressure using a reflux condenser, although lower or higher temperatures can also be used. By working at higher temperatures (using a pressure of at least the vapour pressure of trichlor ethylene) somewhat higher yields are obtained in shorter time.

At all temperatures the dimeric compound preponderates. At lower temperatures the yield of trimeric and higher polymeric compounds the

highest of which show wax-like character is a little better than at higher temperatures.

The part of the starting material which has not undergone polymerization can be recovered by distillation and in a further process be treated with peroxides so that finally practically the whole of the starting material can be converted into polymers.

The lower polymers can be isolated by fractional distillation. They are suitable as non-combustible solvents, diluents, detergents, softening agents, insecticides, isolating materials, especially for electrical purposes, etc. They may also be used for the making of synthetic products.

The following examples illustrate the invention, but the invention is not restricted to the given examples.

Example 1

100 parts by weight of trichlor ethylene are boiled for 45 hours (using a reflux condenser) with 2 parts by weight of benzoyl peroxide. The reaction product may be filtered and the unaltered trichlor ethylene is recovered from the filtrate by distillation at atmospheric pressure. The higher boiling parts are fractionated at 15 mm. pressure, with the following result:

87-110° C.-----	.8 part by weight
110-115° C. (dimeric tri- chlor ethylene $C_4H_2Cl_6$) -	24.1 parts by weight (specific gravity 1.662 at 29° C.)
115-190° C.-----	1.6 parts by weight
190-197° C. (trimeric tri- chlor ethylene $C_6H_3Cl_9$) -	2.9 parts by weight
Solid residue-----	.5 part by weight

The dimeric trichlor ethylene shows a boiling point of 228-229° C. at 762 mm. pressure, a specific gravity of 1.671 at 20° C., an index of refraction n_D of 1.5457 at 20° C. and a dielectric constant of 3.97 at 20° C.

Example 2

100 parts by weight of trichlor ethylene and 2 parts by weight of benzoyl peroxide are heated to 100-115° C. for 15 hours in a closed tube. The unaltered trichlor ethylene is distilled off and the remainder is fractionated at 15 mm. pressure, with the following result:

	Parts by weight
110-114° C.-----	14.1
195-200° C.-----	.5
Solid residue-----	3.2

Example 3

100 parts by weight of trichlor ethylene and 1 part by weight of benzoyl peroxide are heated to 90-100° C. for 7 hours in an earthen vessel being in an iron autoclave, under a pressure of added

nitrogen of 50 atmospheres. The unaltered trichlor ethylene is distilled off and the remainder is fractionated at 15 mm. pressure, with the following result:

Parts by weight 5

100-115° C-----	25.5
190-200° C-----	4.0
Solid residue-----	.5

Example 4

The working is carried out as in Example 1, but instead of 2 parts by weight of benzoyl peroxide 1 part by weight of tetrahydronaphthalene is used. The yield is lower.

WALTER BAUER.

ALIEN PROPERTY CUSTODIAN

METHOD OF PREVENTING SCALE FORMATION

Hiroshi Suzuki, Meguro-ku, Tokyo, Japan; vested
in the Alien Property Custodian

No Drawing. Application filed August 27, 1938

This invention relates to a method of preventing scale formation from sea water, brine, etc., which contain calcium compounds, removing these compounds as calcium oxalate precipitated by means of adding oxalic acid or oxalate into such water. In this invention, the precipitated calcium oxalate is decomposed by alkali carbonate into solution of alkali oxalate and precipitate of calcium carbonate; into the solution thus obtained being added soluble alkali salts such as sodium chloride or sodium sulphate and used repeatedly for precipitation of calcium oxalate from sea water, brine, etc.

The object of this invention is to provide an efficient and economical method whereby scale formation can completely be prevented from sea water, brine, etc., containing calcium compounds.

Scale prevention may be very economically effected if calcium compounds, the essential elements causing scale formation in the course of evaporation of sea water or brine, can be removed from such water simply by sodium carbonate, the scale, however, is not removed completely by this method. On the other hand, scale formation is prevented completely, by means of adding oxalic acid or oxalate into sea water or brine, but this method is so uneconomical that it cannot be practised for industrial purposes owing to the high prices of such substances.

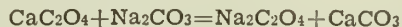
According to this invention, the prevention of scale formation from sea water, brine, etc., can be accomplished economically, by means of removing calcium salts contained in such water, employing oxalic acid or oxalate as a mediator and recovering the soluble oxalate from the precipitated calcium oxalate by sodium carbonate.

If, this recovered alkali oxalate is added directly into sea water or brine, it requires long time for

precipitation of calcium oxalate and reaction is incomplete. These disadvantages can be eliminated, as in the case of the present invention, by means of adding soluble alkali salt such as sodium chloride or sodium sulphate into recovered alkali oxalate before adding it into sea water or brine, resulting in accelerated precipitation of calcium oxalate and shortening of the time required for complete reaction.

An example of this invention is explained in the following description:—

A suitable quantity of oxalic acid or sodium oxalate is to be added into sea water in a vessel, and, it is to be left until the calcium compounds contained in it is precipitated as calcium oxalate. The precipitated calcium oxalate is then to be filtered, and added into water solution of sodium carbonate of equivalent quantity and is boiled for about four hours; thus sodium oxalate and calcium carbonate being produced by the following chemical reaction.



This calcium carbonate is to be removed by means of filtration and small quantity of sodium chloride is to be added into solution of sodium oxalate thus obtained, which is then added into new sea water in order to remove the calcium compounds contained in it, and the procedure is repeated as explained above.

In this invention, the solution of alkali oxalate into which soluble alkali has been dissolved, may be used instead of oxalic acid or oxalate, in the first course of the procedure, in order to remove the calcium compounds contained in sea water, brine, etc.

HIROSHI SUZUKI.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PRODUCING AN AGENT ADAPTED FOR RENDERING MATERIALS IMPERMEABLE

Wilhelm J. H. Hinrichs, Hamburg, Germany;
vested in the Alien Property Custodian

Application filed September 27, 1938

It is known that by the action of aldehyde, for example an aqueous solution of aldehyde, glue is hardened and can be employed for the coating or for the impregnation of containers of paper, pulp, textiles, wood veneer and the like. In this way containers can be obtained which are impermeable with respect to oils and fats of animal, vegetable and mineral origin as well as against aliphatic and aromatic hydrocarbons, for example petroleum, benzine, benzol and the like.

The coatings or impregnations obtained in this manner have however the disadvantage that they are brittle and that they do not remain flexible or creasable. The containers are readily cracked or blistered by shock or pressure and in this way lose their fluid tightness and leak.

It has been found that the hardened coatings consisting of skin glue, bone glue, gelatine, can be given certain good and useful properties and at the same time the above mentioned disadvantages overcome, if mixtures are made which consist of glue and rubber together, and these mixtures utilised as substances for rendering materials impermeable. Rubber solutions of all kinds have been found suitable for this purpose, in particular natural and artificial rubber latices and further dissolved dried rubber latices, other rubber solutions and also artificial materials of rubber-like properties, in particular those embodying vinyl polymers.

A difficulty in the production of such mixtures comprised of hardened glue and rubber latex or aqueous dispersions of artificial materials is found in the fact that rubber latex and the other dispersions are very sensitive towards heat and also on admixture with other materials very readily coagulate and separate, whereby the mixture is rendered unusable. In order to avoid these disadvantages the glue must be first so treated that it is cold soluble. Also on addition of the hardening materials to the solution of the cold soluble glue and the admixture with the rubber dispersion great care must be taken.

The liquid material composed in the stated manner may be readily applied as coatings by hand or by machine and gives products which after subsequent drying on paper, pulp, textiles, wood veneers and so forth, gives films resistant against and impermeable to oils of any kind, petroleum, benzine, benzol, chemical compounds such as thio-ethers and such like organic sulphur compounds their solutions in benzol and the like and, which may be used in the stated manner to treat endless webs of paper, pulp, textile and so forth, from which container sections can

be stamped out. The individual parts stamped out, namely walls, bottoms, covers and so forth can be glued together by the use of the material according to the invention in such manner as to be impermeable to oil, petroleum and benzol.

A particularly surprising property of the material according to the invention is to be found in the fact that, in spite of its content of rubber or its substitutes, the quantity of which corresponds to the quantity of glue present, it is insensitive towards oils, fats and solvents consisting of hydrocarbons whereas rubber is immediately dissolved or destroyed thereby.

A mixture having the desired properties consisting of glue with rubber or rubber substitutes in solution from which raw materials and containers impermeable to oils, fats, benzol, benzine, and so forth can be obtained, can be prepared, for example, in the following manner.

Skin glue is allowed to swell for a few hours in water and an aqueous solution of nitrogen base (amine and/or ammonia), for example ammonia, until the glue is saturated with the aqueous solution and has attained its most swollen condition. The container during this is continuously closed. The glue is then transferred to a water bath and warmed gently until completely dissolved. This is effected at a relatively low temperature of below 30° C. A formaldehyde solution is then added to the ammoniacal glue solution with stirring. As the result of the chemical reaction of the mixture a considerable heating results.

The solution of the glue can, at least in part, also be so effected that it is first warmed with addition of water or without any water addition on the water bath and the aqueous solution of the nitrogen base, or the nitrogen base and the water subsequently added. Aldehyde is then introduced.

The glue is cooled down with continual stirring in order that it shall not gelatinise prematurely at the walls.

In another container, for example 150 parts of a purified rubber latex freed from its unsuitable constituents by centrifuging and simultaneous washing with ammoniacal water, and having 60% rubber content is diluted by mixing with 100 parts of water.

This aqueous rubber latex which is stabilised with a small proportion of ammonia is brought as far as possible to the same temperature as the glue solution. The temperature of both the parts to be admixed lies preferably below 50° C., since the rubber solution is sensitive towards higher

temperatures and at higher heats undesired evaporation losses can occur. Preferably the temperature of both mixtures lies between 20 and 30°C. Temperature differences of about 2 to 3°C. are without influence upon their satisfactory combination. Higher differences act unsatisfactorily by giving a greater tendency to the rubber dispersions to coagulation.

The glue solution and the rubber latex which are both adjusted for example to 24°C. are combined with one another with continual stirring and form the product according to the invention for rendering materials impermeable. In order to avoid coagulation, it is recommended to add the glue solution to the rubber latex.

The product according to the invention may have, for example, the following composition:

20 parts of water
 25 parts of an aqueous 25% ammonia solution
 10 parts of skin glue
 30 parts of an aqueous 30% formaldehyde
 15 parts of a 60% latex concentrate freed from its hygroscopic and unsuitable constituents by centrifuging and simultaneous washing with ammoniacal water.

According to the desired properties and purposes of use of the product, the proportions of the constituents can be altered. If the ammonia addition is increased above the content of formaldehyde then there is obtained a lower viscosity of the product but at the same time, however, a reduced hardening. The film then obtained for example on paper is less resistant and impermeable to petroleum, oil and so forth. If the content of formaldehyde is increased over the content of ammonia, then there is obtained a higher viscosity of the product combined with a relatively better impermeability of the film obtained therefrom against oil, petroleum, benzol and so forth.

The product can be kept in closed vessels and the like for several weeks without the films obtained therefrom varying essentially in their resistance. A longer storability can be obtained, however, if one or a few days after the production a further proportion of the aldehyde employed is introduced in aqueous solution with stirring, for example, 15%. In the interim, the intramolecular conversion has so far proceeded that the mixture is ready to receive a further

proportion of formaldehyde without being unfavourably influenced.

The product obtained in the described manner remains liquid down to a temperature of about 21°C. and gelatinises at about 18°C. and below. According to the composition, the gelatinisation temperature can however lie considerably lower. By careful slow warming to about 24 to 25°C. the solid mass can again be rendered liquid. On reliquefaction a higher viscosity is obtained at lower ranges of temperature, for example 23 to 24°C. and a corresponding lower viscosity at a somewhat higher range of temperature, for example 28 to 30°C. In this condition the product is outstandingly suitable for application by brushes, rolls, spraying devices and the like to paper, pulp, textiles and veneers both in the form of sheets and also in endless webs and further to objects such as walls and the like for the coating (for example dipping) of containers of materials of all kinds for the production from textiles or other materials of coverings resistant and impermeable to oil and petroleum for oil conduits, bags and so forth.

By simple coating (dipping) with the product, for example paper containers even up to the size of barrels can be rendered suitable for the handling and shipping of oils, fats, petroleum, benzene, benzol, oil colours and so forth.

Instead of skin glue or bone glue use may also be made, with the same results, of cold soluble adhesive albumen materials obtained from albumen, casein or vegetable albumens, for example soya casein, by treatment with ammonia. These adhesive materials are in each case treated with formaldehyde as hardening agent and with an aqueous dispersion of rubber or rubber-like artificial materials for example vinyl condensation products or polyvinyl compounds. For increasing the storability and handleability prior to the production of the coating and impregnation, it is also advantageous with products obtained from these glue materials to add a further quantity of aldehyde a few days after the combination of the glue material with the rubber dispersion.

As soon as the product is applied and the coating and impregnation dried it is of great permanence.

WILHELM J. H. HINRICHS.

ALIEN PROPERTY CUSTODIAN

PLASTIC COMPOSITION AND PROCESS FOR
MANUFACTURING THE SAME

Henri Carroll, Paris, France; vested in the
Alien Property Custodian

No Drawing. Application filed October 15, 1938

The present invention has for object a new composition comprising several products acting as colloids under the influence of temperature and of pressure and the mutual affinity and solubility of which relatively to each other allow of obtaining at the same time a plastic material having new properties and given original characteristic features; the invention also relates to the process for manufacturing said plastic composition.

This new plastic, waterproof, fire-proof, dielectric composition can present characteristics of resistance and of hardness which differ according to the nature of the charges employed; it can also be directly metallized without previously scouring the surfaces to be treated, according to known processes.

The process allowing to carry out the invention consists:

(1) In incorporating with the solid charge dispersed in a liquid, several plastic compounds in the soluble state.

(2) Then in rendering the latter insoluble by double decomposition by means of a metal salt, for instance, an alumina or magnesia salt, or, preferably, a mixture of these two salts.

(3) After elimination of the residual liquid, the insoluble mass is dried in a stream of hot air, then pulverized and eventually mixed with coloured mineral pigments insoluble in the solvents subsequently used.

(4) The dry powder thus obtained is treated with a liquid constituted by a mixture of suitable solvents containing in solution therein a mixture of thermoplastic products the affinities of which (for instance their solubility relatively to each other, their melting point) allow them to combine with the insoluble plastic materials impregnating the solid charges mentioned in the first operation.

(5) The organic dye-stuffs eventually necessary, being dissolved in the solvent or solvents.

(6) The solvent or solvents are then eliminated by distillation.

The powder finally obtained presents original characteristic features, particularly physical and mechanical properties very different from those of the plastic constituents taken separately.

The moulding of this powder is effected at temperatures comprised between 125 and 180° C. at a pressure of 95 to 125 kilograms per square cen-

timeter, the duration of the baking operation varying between 2 to 5 minutes according to the bulk of the article to be moulded.

The constituents of this plastic material are for instance:

I. A charge constituted: (a) by mineral products, preferably, by silicates of alumina and of magnesia in powder form, such as pulverized slate and asbestos fibre, and (b) by cellulose products such as cork powder.

II. Organic materials rich in animal proteins such as casein, or vegetable proteins such as peanut cakes, to which are added natural resin, naphthenic acids or a mixture of stearic and oleic acids.

These compounds being rendered soluble in the hot state in water to which soda has been added, are then precipitated by double decomposition, by means of a solution of an alumina or magnesia salt or of both these salts.

III. A mixture of two thermoplastic products such as:

(a) Glycerophthalic resin or cresylic resin either of which is modified by natural resin or chlorinated rubber.

(b) A resinate of glycerine (ester).

The products included in paragraphs II and III have mutual affinities and physical and chemical characteristics such that, under the action of heat and of pressure used for moulding, they act as colloids and give a new product having definite properties.

The following composition is given by way of example:

	Per cent
Cork powder.....	52
Asbestos fibre.....	3
Slate powder.....	8
Natural resin.....	5,3
Naphthenic acids.....	5
Caustic soda.....	0,7
Casein	12
Glycerine resinate.....	8
Glycerophthalic resin modified by natural resin	6
	100

The above composition can, of course, be modified according to the properties it is desired to obtain in the plastic products. For instance, for

sheets or plates which must have great resistance to penetration, the charge will be constituted by the powder of a wood of high density and the proportion of the thermoplastic products will be lowered relatively to that of the plastic products used for impregnating the solid charges.

On the contrary, for the moulding of articles having vertical walls of small thickness, it is advantageous to use a composition containing a slightly greater proportion of thermoplastic products in order to allow the heated plastic powder subjected to pressure to more rapidly penetrate all the cavities of the mould.

The process for the manufacture of this plastic composition being an object of the invention, the latter is briefly described hereinafter, by taking as a basis, by way of example, the above mentioned composition.

In a vat heated for instance by steam circulating in a double casing, are introduced the water, soda, natural resin, naphthenic acids and casein, then the mass is raised to a temperature approximating boiling point, the liquid being thoroughly stirred by a turbo-mixer, the mineral and cellulose charges are added; when the latter are well impregnated and maintained in suspension in the liquid, a boiling solution of sulphate of alumina and of magnesia is gradually poured in, until complete double decomposition; the residual liquid being eliminated, the charges impregnated with insoluble products are washed, then the divided mass is subjected to a stream of hot air until complete dehydration.

The dry product to which has been eventually added the coloured mineral pigments, is crushed into a powder, then treated with the solution of the solvents containing in solution therein the thermoplastic products and, eventually, the dissolved organic dye-stuff.

The solvent being eliminated by distillation in a closed vessel, the plastic powder is ready to be used for the moulding of articles by heating under pressure as previously indicated.

It has been stated above that use can be made of organic materials rich in animal proteins or vegetable proteins; the composition previously indicated utilised animal proteins such as casein, which necessitated the use of various other constituents; the use of vegetable proteins allows of simplifying the manufacture and of utilising a smaller number of constituents: as vegetable proteins use is made of pea-nut cakes or rice flour, or a mixture of both.

These products rich in proteins have remarkable plastic properties and intimately combine, even in small proportions, with synthetic resins mixed with a high proportion of charges such as cellulose waste, they are capable of being moulded in the hot state and under low pressures in order to give moulded articles having interesting characteristic features as well from a dielectric standpoint as regarding impermeability and mechanical resistance.

The following composition, given hereinafter by way of example, gives the desired results:

Cellulose materials (moulded paper pulp, wood flour, etc.)	31,20
Pea-nut cakes	47,20
Trisodic phosphate	1,60
Cholesterol	0,30
Cresylic resin	19,70
	100

In this example the charge is constituted by cellulose materials, but use can just as well be made of the charge mentioned in the preceding example, or of any other materials constituting the charge.

This composition gives a plastic powder which can be moulded under a pressure of 75 kilograms per square centimeter at a temperature of 165° C.; the duration of the baking being about 1 minute 30 seconds for thicknesses of 2 millimeters.

The moulded articles have a polished appearance and are waterproof and fire-proof: trials effected on test-pieces made according to this composition, have given a dielectric rigidity of 34,000 volts for a plate having a thickness of 1 millimeter; the rupture load is 2 kilograms, 65 per square millimeter and the resistance to shocks has given with CHARPY'S pendulum a resiliency of 8,1 per square centimeter; furthermore, the moulded product can be readily drilled, threaded and turned.

In this example of realisation with materials rich in vegetable proteins, the impregnation of the charge can take place without rendering the products insoluble by double decomposition by means of a metal salt. The following method of procedure is then adopted: the impregnation of the charge is obtained by mixing pea-nut cakes or rice flour with the cellulose charge (paper waste, moulded paper pulp, wood flour, etc.) in presence of water to which is added either trisodic phosphate, borate of sodium or ammonium for rendering the proteins soluble in water.

The paste is kneaded and coloured pigments are added thereto, then it is dried in a stove and finely crushed. Cholesterol, acting a plastifying agent is incorporated with this powder. Then cresylic resin is added which is separately prepared and obtained either in the liquid or in the solid state and in which have been previously dissolved soluble dye-stuffs; thus, an intimate mixture is obtained of the plastic powder and the cresylic resin which is in small proportion, about 20%; if the resin is in the liquid state, it will be mixed with the powder and the whole will be kneaded and crushed in the hot state; if the resin is in the solid state, it will be necessary to dissolve the resin in a solvent in order to incorporate it with the powder and the solvent will be subsequently eliminated.

HENRI CARROLL.

ALIEN PROPERTY CUSTODIAN

RESIN-LIKE RUBBER CONVERSION PRODUCTS

Arthur Greth and Johannes Reese, Wiesbaden, Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 1, 1938

This invention relates to the production of isomerization products of rubber and rubber-like products whereby rubber conversion products are obtained having resinous properties, such products being suitable for many uses throughout the arts.

A process has heretofore been formulated for the conversion of rubber into resin-like products by subjecting rubber to the action of phenols and acids which do not form compounds with phenols, or salts capable of inducing isomerization, such process being carried out by heating unvulcanized or vulcanized rubber while in admixture with one or more phenolic compounds and with the isomerizing agent or catalytic agent for a relatively short reaction period at a temperature up to, but not higher than, the boiling point of the phenolic component present.

An object of the present invention is to improve upon this process by increasing its efficiency and by improving the properties of the resin-like conversion product obtained.

In accordance with the process of the present invention, the conversion of the rubber compound through the action of the phenolic agent and the isomerizing agent is effected at temperatures higher than the boiling point of the phenolic agent employed. In order to carry out the conversion process at such temperatures, the process is effected in an autoclave wherein a superatmospheric pressure exists. The use of superatmospheric pressure also serves to assist the conduct of the reaction.

Through the use of the process of the present invention, the reaction time is lessened to a considerable degree and the amount of isomerizing agent or catalyst required is reduced to a substantial degree. The conversion reaction which brings about the isomerization of the rubber material treated, forming the resin-like rubber product, is aided by the increased reaction temperature and also by the consequent shorter reaction period required, for side reactions serving no useful purpose, and resulting from the longer reaction period as heretofore employed, are strongly repressed or are practically prevented from occurring. Through the use of the instant process, it is possible to obtain a very homogeneous final product having improved or superior properties.

In accordance with an important embodiment of the present invention, the conversion reaction is carried out in the substantial absence of water. Unless special effort is made to operate in the absence of water, such compound will be unavoidably brought into the reaction mass in the

various raw materials employed, including the phenols or the rubber or the isomerizing agent. It has now been discovered that the presence of water in many instances has a decided detrimental effect upon the process. The water may be removed from the raw materials in any one of a number of ways, but in accordance with a very satisfactory method, constituting a feature of one embodiment of the invention, an excess of phenol is introduced into the initial mixture before the start of the actual conversion and the mixture subjected to distillation to remove its water together with the excess of phenol, after which the heating is continued to bring about the isomerizing reaction. The removal of water in this manner is of advantage to the isomerizing process whether the conversion be effected below or at the boiling point of the phenolic component or at a temperature above the boiling point with operation under superatmospheric pressure.

In accordance with another embodiment of the present invention, the isomerizing reaction is carried out in the substantial absence of oxygen. It has been discovered that the presence of oxygen or other oxidizing agents have a depolymerizing and decomposing effect upon the rubber treated or the rubber product formed, and now also that the influence of any oxygen present is detrimental to the instant isomerizing reaction of the process of the instant invention. This discovery indicates that the instant conversion process is quite different from the decomposition of rubber due to the catalytic effect of oxygen. The oxygen is preferably removed from the reaction mixture by passing an inert gas, such as carbon dioxide, nitrogen or the like therethrough. This treatment improves the conversion reaction and decreases the time required for the reaction. It is therefore advantageous to operate the instant process in the presence of an inert gas after the removal of oxygen, the advantages being obtained whether the conversion be effected under normal pressures or under raised pressures.

The instant process is not only applicable to the treatment of natural rubber and vulcanized products thereof, but is also suitable for the treatment of synthetic rubber or rubber-like compounds prepared from polymerized hydrocarbons, as for example, the product known as Buna. Other raw materials include Neoprene, and Duprene. Isomerizing agents or catalysts found to give excellent results comprise borohalide compounds or the halogen derivatives of boron, such as borofluoride, and also compounds

thereof, such as borofluoride acetic acid. These catalysts are preferred not only because of their effectiveness in causing the reaction to proceed but also because of their fluid nature, which permits them to be easily removed from the reaction mixture.

The purification of the reaction mass to separate the phenolic reaction medium and the catalyst from the resin-like reaction product may be effected in several ways. In accordance with one method, the phenolic material is removed by direct distillation, preferably with the aid of a vacuum and with agitation. The distillation may also be carried out with the aid of steam. Further separation may be brought about by the action of mechanical working devices, such, for example, as rollers or kneaders.

In accordance with another method, the undesired materials may be separated by grinding the reaction mass in a ball mill in the presence of a solvent for the phenolic material, such for example, as a solution of an alkali metal hydroxide or an alcohol. Then the reaction mass in the dissolved state may be extracted by a treatment with those substances which dissolve the phenolic component or the catalyst or both of such components, suitable solvents being solutions of caustic soda. Alternatively, such solutions may be distilled over with the aid of other volatile substances which assist in the evaporation of the phenolic component.

In accordance with other processes for purification, solutions of the reaction mass may be treated with liquid materials that dissolve the phenolic component but which do not dissolve the rubber conversion product. In working with substances which do not dissolve the rubber reaction product, the direct application of such solvents has been found quite effective. Substances suitable for such treatment are those containing alcoholic groups, but which have little or no solvent power for the rubber substances at normal temperatures, or those which have the power to dissolve such substances only at elevated temperatures. Under this procedure, it is possible to wash out the phenolic component and the catalyst by using alcohols, the boiling points of which are above the softening point of the resin component, examples of the alcohols being butyl alcohol, amyl alcohol, hexyl alcohol or cyclohexanol, which are mixed with the resin product with the aid of heat and of stirring, kneading or trituration.

In accordance with another but important embodiment, the separation is effected through the use of substances possessing boiling points below the softening point of the resin product. When these substances are used, it is necessary to work under superatmospheric pressure. The resin-like product treated in this manner can be freed of the phenolic component much more easily, since the mass is in the form of a liquid permitting more intimate contact with the washing medium.

The resin-like rubber products produced in accordance with the instant invention, depending upon the conditions under which they are produced, may be obtained in granulated form, in the form of a powder, or, after being melted, in the form of a resin. The resin-like product may be used in industrial applications as such, or it may be combined with any number of various substances. For example, they may be added to various oils and lacquers, or, such binding agents may be added to them. The resin-like products may be compounded advantageously with natural resins or with synthetic resins, especially with

alkyd resins, other rubber products or caoutchouc derivatives such as the halogen-caoutchouc or with bitumen, pitch, wax, cellulose derivatives, fillers, dye stuffs, lubricants and other compounds. The resin-like products may be applied in undiluted form, in solution or in emulsified form. Such products may be used to produce protective coatings or finishing coatings to materials of many kinds, including threads, wires, ropes, bands, films and foils. They may also be used as adhesives, as adhesive layers, as sizing or finishing materials for textiles, as impregnation materials, as binding agents for layers of materials and as pressing and spraying materials. In the following illustrative examples, all parts are given by weight.

Example 1

2.5 parts of rubber, through which carbon dioxide has been passed is introduced into a stirring autoclave together with a mixture of 5 parts of phenol and 0.2 parts of orthophosphoric acid through which nitrogen has been led when in a fluid state. After causing the reaction mixture to liquefy at ordinary pressure and feeding carbon dioxide therethrough, 0.5 parts of phenol is distilled therefrom. This distillation treatment removes the water content of the reaction mixture. The autoclave is then closed and the temperature raised to 210° C. With good stirring the conversion of the rubber will have taken place within 1 to 2 hours. The reaction mass, from which a part of the phenol and a greater part of phosphoric acid will have settled to the bottom, is removed from the reaction container by the use of pressure. The raw product of the conversion reaction, which is a solid solution of phenol and rubber conversion product in substantially equal proportions, is heated in twice its volume of ethyl alcohol in a pressure container to about 140° C. and thoroughly stirred. The phenol-alcohol mixture is then separated from the rubber resin, and the extracting is repeated about 4 to 5 times, or until the phenol content of the rubber resin is less than 0.2%.

The phenol- and acid-free alcohol containing conversion product is ground in a closed mill and dried. In its powdered form it is a coarse, almost white powder.

Example 2

1 part of Buna 85 after being cut into small pieces is added to 5 parts of a cresol mixture (meta and para) to which 0.05 parts of borofluoride acetic acid have been added and the mixture is heated in a closed container to 200° C. while being stirred. After several hours, the conversion of the rubber is sufficiently complete and the cresol solution present is worked with alcohol until no further precipitate results. The precipitated rubber substance is then dissolved in twice its volume of toluol and is again precipitated with alcohol. A phenol-free product is obtained by successively dissolving and precipitating four times. This product is freed from the absorbed and occluded alcohol by spraying it in an evacuated chamber, the final product being obtained in a finely divided form.

The production of resin-like products by the action of phenols and catalytic agents at temperatures up to the boiling point of the phenolic component is described in the earlier co-pending application, Serial No. 147,479, filed June 10, 1937.

ARTHUR GRETH.
JOHANNES REESE.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR STABILIZING CELLULOSE ESTERS

Aladar Schuller, Antwerp, and Remi-Gustaaf Tritsmans, Mortsels, near Antwerp, Belgium; vested in the Alien Property Custodian

No Drawing. Application filed November 25, 1938

Our invention relates to cellulose esters and more especially to the stabilization of solid organic acid esters of cellulose in accordance with our copending application for patent Serial No. 64,793, of which the present application is a continuation-in-part.

As is well known, cellulose esters as prepared from cellulose and organic acids or acid anhydrides in the presence of catalysts and solvents or agents preventing solution, are subject to decomposition and not stable. More especially the sulfuric acid, which is the most widely used catalyst and which combines with the cellulose, forming mixed cellulose sulfate esters, is known to greatly impair the stability of the organic cellulose esters, such as the acetates, propionates and butyrates, from which films and other photographic materials are prepared.

A great many suggestions have been made regarding stabilization of such esters, but none of them has been found altogether satisfactory. More especially washing of the esters with water and dilute acids at normal or increased pressure has been found useless because at ordinary temperature these washing agents remain substantially ineffective for the purpose in view, while at elevated temperature they exert a saponifying action on the cellulose esters whereby these latter are impaired. Treatment with aliphatic acids or alkyl esters of such acids at elevated temperature has been found to also injure the cellulose esters. Methyl alcohol as such or mixtures of this alcohol with water, mineral oil products, benzol or carbon tetrachloride, when contacted with cellulose esters at ordinary temperature have not been found capable of imparting to cellulose esters the stability required to render them fit for use in the manufacture of photographic materials.

We have now found that all esterified organic esters of cellulose and quite especially cellulose triacetate, however also mixed esters, can be stabilized in a highly satisfactory manner by treating them at an elevated temperature, preferably above 50°C and better still at temperatures in the neighbourhood or above 100°C, however preferably not beyond 140°C, with an organic liquid and more especially with an aliphatic and/or aromatic hydrocarbon, an alcohol, a ketone, a derivative of such a compound or a mixture of two such compounds, which at these temperatures does not suffer decomposition with the liberation of an acid or alkali, is inert with respect to and does not dissolve the organic cellulose ester, such as for instance cellulose triacetate and renders

the liberated acid, for instance sulfuric acid, innocuous by entering into chemical combination with it.

We may also employ low boiling organic liquids, provided that under a pressure above normal they remain liquid, stable and inert with respect to the cellulose esters under treatment.

Benzol, toluene, xylene, methylalcohol, ethylalcohol, propylalcohol, butylalcohol, amylalcohol, benzylalcohol, glycol, glycerine, methylethylketone, diacetonealcohol, methylcyclohexanone and commercial benzine have been tested and found useful as stabilizing agents at temperatures ranging between about 50° and 140°C, under and above normal pressure, the cellulose ester, such as cellulose triacetate, if treated for a sufficient period of time, on being heated one hour to 230°C, substantially retaining its color.

We have found that the treatment according to this invention is not by any means a mere washing process. For while free sulfuric acid can be extracted by washing, the mixed cellulose sulfate esters formed during esterification of cellulose in the presence of sulfuric acid cannot be washed out. We feel certain that it is the elevated temperature which is responsible for the stabilizing effect obtained by our treatment, in that the mixed cellulose sulfate ester is decomposed at this temperature and the sulfuric acid is set free so that it can be bound by chemical reaction and removed by washing.

We have further found that the absolute temperature at which this stabilizing treatment is carried out, plays an important rôle in that it determines the duration of this treatment. Thus, when using methylalcohol which under normal pressure boils already at 60°C, five hours boiling was required to render cellulose triacetate practically stable. With ethylalcohol, boiling at 80°C, a four hours treatment is required, while propylalcohol, boiling at about 110°C, will stabilize the ester after three hours.

A typical example of the influence of the temperature on the result of this treatment is the following: A cellulose triacetate, after two hours boiling in xylene at 60°C, on being heated one hour to 200°C, showed an appreciable brown coloration, while, when treated with xylene two hours at 130°C, one hour's heating to 200°C did not in any way change the pure white color of the ester. This shows clearly that it is the heat that is the principal factor, which fully agrees with the theory advanced by us that stabilization will be obtained only if the mixed ester which contains the radical of the catalyst acid, such as the or-

ganic cellulose sulfate ester, is decomposed and the catalyst acid, such as sulfuric acid, set free so that it can be bound by chemical reaction and removed by washing.

The upper temperature limit is determined by the temperature up to which the material to be stabilized may be heated without being affected detrimentally.

Our findings also account for the fact that with the liquids mentioned above, for instance with methylalcohol, when applied at normal temperature, no adequate degree of stability is obtained even if they are allowed to act on the cellulose ester several days. If cellulose triacetate is treated with methylalcohol at 70°C, adequate stability is obtained only after 6 hours, whereas at 120° C the same degree of stability is reached already after some minutes.

This interrelation between the temperature and the length of time required for stabilization enables use to adapt our process to the particular nature of the material to be treated. Cellulose esters which are injured when exposed to a high temperature, are stabilized at a correspondingly low temperature in a correspondingly longer period of time, while others which are less sensitive to heat, may be stabilized at a higher temperature and in a correspondingly shorter period of time.

In every case the results obtained are the better and more reliable, the higher the temperature of treatment and it is therefore advisable to operate at as high a temperature as possible in each individual case. However, when stabilizing cellulose triacetate, the temperature should not substantially exceed 130°C, since at 140°C decomposition would set in.

We have found benzol and ethylalcohol to be particularly suitable as stabilizing liquids, since these substances are available at low cost and do not in any way affect cellulose esters at temperatures such as may be used in our process.

If it should be desired to use low boiling liquids, for instance in order to enable the stabilized product to be dried rapidly at low temperature, the stabilizing treatment should be carried through in a closed vessel, i. e. under pressure above normal and consequently at a higher temperature.

The stabilizing liquid may be recovered by distillation with steam.

Examples

1. 100 parts by weight cotton cellulose are

treated with a mixture of 400 parts acetic anhydrid, 200 parts acetic acid and 5 parts sulfuric acid. After acetylation some water is added, whereafter a maturing period of several hours is interposed, followed by precipitation and washing with water. The diacetate obtained is then introduced, for the purpose of stabilization, into about eight times is quantity of ethylalcohol, and left therein for six hours at a temperature of 70°C. This is followed by centrifuging and drying. The diacetate thus treated is of excellent stability. A sample of the acetate, when heated one hour at 200°C, does not show any brown discoloration.

2. 100 parts cotton cellulose are treated with a mixture of 600 parts acetic anhydrid, 1000 parts benzol and 2 parts sulfuric acid. Acetylation is followed by centrifuging and washing out with benzol. The product is cellulose triacetate in fibrous state. The still unstable product is placed in a container and 1200 parts benzol are added. The container is then closed hermetically and heated to about 120°C, the internal pressure being thereby raised to about 3 atms. After two hours the liquid is drained off and the traces of benzol expelled from the triacetate with steam. The triacetate now possesses the same stability as the product obtained in accordance with example 1.

3. 100 parts triacetate obtained in accordance with example 2 are heated with 900 parts methylalcohol to about 110°C in a closed vessel, the internal pressure rising to about 4.5 atmospheres. After a 3 hours treatment the liquid is run off and the adhering methylalcohol centrifuged and washed out with water. This product when subjected to the stability test by being heated to about 200° C, does not turn brown even after an hour.

4. 100 parts cotton cellulose are treated with a mixture of 400 parts acetic anhydrid, 200 parts butyric acid, 3 parts sulfuric acid and 1000 parts toluene. The esterification-product, a mixed ester in fibrous state is treated, after centrifuging and washing out with toluene, four hours with 1000 parts toluene at 90°C. The product thus obtained, when heated one hour to 200°C, retains its white color.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

ALADAR SCHULLER.

REMI-GUSTAAF TRITSMANS.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PREPARING KETENES

Richard Hueter, Dessau-Rosslau/Anhalt, Germany; vested in the Alien Property Custodian

Application filed November 29, 1938

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This invention relates to processes for the preparation of higher molecular ketenes from the halogenides of higher molecular carboxylic acids by treating said halogenides with strong tertiary bases.

The ketenes obtained as a reaction product in the instant process form valuable intermediate products suitable for a large variety of organic chemical synthesis. They are especially valuable as acylating agents for all organic compounds which contain an active hydrogen atom as, for example, amines, hydroxy compounds, and their substitution products. Among the various compounds containing active hydrogen atoms may be mentioned beta-hydroxy-ethane-sulfonic acid, beta-methyl-amino-ethane-sulfonic acid, and the like. In addition to being reactive with the compounds containing active hydrogen atoms, the ketenes may also be used as addition agents for introduction at the double bonds of various organic compounds.

As raw materials for the processes of the present invention, one uses the halogenides of carboxylic acids, particularly the chlorides of aliphatic, cycloaliphatic, and fatty aromatic carboxylic acids, including both mono- and polybasic acids. As illustrative of the various types of carboxylic acids mention may be made of caproic acid, lauric acid, palmitic acid, oleic acid, montanic acid, naphthenic acid, nuclear alkylated aryl fatty acids containing at least one alkyl group, adipic acid, sebacic acid, cyclohexane diacetic acid, and the like. The hydrocarbon chains of these carboxylic acids may be interrupted by known hetero atoms or hetero atomic groups, as for example, oxygen, sulfur, and the like.

While a large variety of halogenides of higher molecular carboxylic acids may be used in the processes of the instant invention, it has been found that the halogenides of fatty acids containing at least 6 carbon atoms in the molecule are particularly suitable and produce especially desirable products. In accordance with a preferred embodiment, it is the practice to carry out the reaction with the strong tertiary bases in the presence of inert water-free solvents although it has been found that the reaction will take place in the absence of solvents.

Among the strong tertiary bases that are illustrative of those usable in accordance with the present invention are the trialkyl amines, such as trimethyl amine, triethyl amine, tripropyl amine, and the like, as well as alkylated ethylene

diamine, alkyl piperidine, and like bases containing trivalent nitrogen.

When the treatment of the carboxylic acid halogenides with these bases takes place in the presence of water-free inert solvents, it is desirable to select solvents of a kind that the hydrohalogenides, such as the hydrochlorides, of the bases which are formed by the reaction are insoluble therein. If this selection is made, a simple separation of the reaction components is possible after completion of the reaction. Solvents of this type are, for example, carbon disulfide, and benzene, other organic solvents being also suitable. As previously stated the reaction can also be carried out in the absence of solvents, and it may in either case take place at normal or elevated temperatures.

The usual method for recovering the ketenes involves a separation of the hydrohalogenide of the base formed in the reaction by filtration and then evaporating the solvent from the filtrate in order to isolate the ketenes. The bases can be recovered from the hydrohalogenide in accordance with known procedures.

Many modifications in the processes of the instant invention will occur to those skilled in the art so the examples, in which the parts occur by weight, are to be considered purely as illustrative of preferred embodiments of the invention.

Example 1

Twenty one and nine tenths parts of the chloride of lauric acid is dissolved in 200 parts of freshly distilled carbon disulfide. To this solution one rapidly adds 101 parts of freshly distilled triethylamine while excluding the moisture of the air, and permits the mixture to stand for 24 hours. Thereupon, the triethylamine hydrochloride formed (13 parts) is filtered off. The filtrate consists of a 9% to 10% solution of decylketene. The ketene can be obtained by careful evaporation of the solvent from the filtrate, if practicable with the exclusion of air. The ketene remains in the form of an oily mass which slowly crystallizes at room temperatures. If the ketene is heated with alcoholic potassium hydroxide it forms potassium laurate.

Example 2

Two hundred and seventy five parts of the chloride of palmitic acid is dissolved in 300 volumes of dry benzol, and after the addition of 10 parts of triethylamine is allowed to stand for 24 hours. The triethylamine hydrochloride which separates therefrom is filtered off. The tetra-

decyl ketene so formed is isolated from the solution in the manner described in Example 1.

It should be understood that the present invention is not limited to the specific examples and illustrations of the compounds and the processes herein disclosed, but that it extends to all equivalent compounds and processes which one skilled in the art would consider within the scope of the appended claims.

In addition to the above named strong tertiary bases there are other bases especially of the higher molecular and mixed series, which may be used for making the prescribed process. Such

strong tertiary bases are e. g. diethyl-propyl-amine, dimethyl-lauryl-amine, dimethyl-oleyl-amine, dimethyl-cyclohexyl-amine, dioctyl-benzyl-amine, N-ethyl-piperidine, N-decyl-piperidine, N-octadecyl-piperidine, N-ethyl-quinoline, N-octyl-quinoline and like bases.

Furthermore instead of the chlorides of carboxylic acids used as initial materials for the prescribed process bromides and iodides of the carboxylic acids may be used. However the bromides and iodides have only a smaller practical interest.

RICHARD HUETER.

ALIEN PROPERTY CUSTODIAN

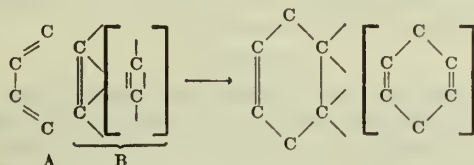
CONDENSATION PRODUCTS

Kurt Alder, Cologne-Deutz, and Hans-Ferdinand Rickert, Cologne, Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed December 17, 1938

The present invention relates to new condensation products and to the process of preparing the same.

The so-called "diene-synthesis" resides in the addition of compounds containing two conjugated C=C double linkages with such compounds containing an ethylene or acetylene group wherein the said unsaturated linkage is likewise conjugated with another double bond. In general, the "diene-synthesis" proceeds in the following manner:



it being to be understood that in the reaction component designated by symbol B the unsaturated linkage is activated by another double bond as stated above. Examples for compounds of type B are 1,3-dienes, α,β -unsaturated aldehydes, ketones, carboxylic acids and carboxylic acid nitriles.

The present invention is based on the observation that the "diene-synthesis" is not restricted to the situations as defined above. We have found that certain unsaturated compounds containing a single C=C double linkage which is not activated by another unsaturated bond, are likewise capable of forming addition products of the character described, if reacted upon with compounds containing two conjugated C=C double linkages. Starting materials of the first type are vinyl esters of organic acids, vinyl halogenides, dihalogen and trihalogen ethylenes. Compounds of the latter type are those commonly employed in the diene-synthesis such as butadiene-1,3, isoprene, 2,3-dimethylbutadiene-1,3, cyclopentadiene, cyclohexadiene and anthracene.

The reaction is performed by simply heating the mixture of the starting materials, preferably in a closed vessel. As a matter of fact care must be taken that the reaction is performed under such conditions as to prevent any substantial polymerization. To this end, polymerization inhibitors such as hydroquinone, pyrogallol and the like may be added to the reaction mixture, particularly in case of working with butadiene-1,3, isoprene and 2,3-dimethylbutadiene. As stated above, the reaction is performed at an elevated temperature, it being impossible to give

definite lower and upper limits, since the optimum reaction conditions depend on the nature of the starting materials and on the tendency of the butadienes and the like to form dimeric products. In general, the dimerization process occurs more slowly than the addition of the 2 reaction components. On the other hand, some of the dimeric products may be split up into the monomeric products at a high temperature, whereas the addition products formed by the interaction of the 2 reaction components are stable at such temperatures. Thus, in case of cyclopentadiene the reaction is preferably performed at 180°C as at this temperature the dimerics are split up so that the addition process is nearly quantitative. Other dienes such as anthracene do not show any tendency to form dimerics at the usual reaction temperature.

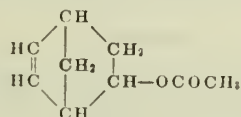
The following examples illustrate the present invention without, however, restricting it thereto, the parts being by weight unless otherwise stated:—

Example 1

100 parts of freshly distilled monomeric cyclopentadiene and 150 parts of vinyl acetate are heated in an autoclave for 14 hours to 180–190°. After distilling off at normal pressure the excess vinyl acetate, the reaction mixture is subjected to distillation in vacuo. At 11 mm pressure the following three fractions are obtained:

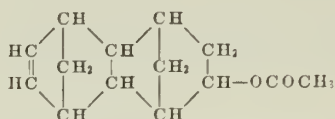
	Parts
I: 73–77°	100
II: 77–140°	10
III: 140–150°	48

Fraction I represents the addition product of the components in the proportion 1:1. It has an intensively ester-like smell and corresponds to the following constitution of a Δ^3 -norbornylene-ol-1-acetate:



By saponification there is obtained the hitherto unknown alcohol, viz. the Δ^3 -norbornylene-ol-1 of the melting point 108–109°. The hydrotriazole prepared therefrom by the addition of phenylazide has the melting point 147–148°. By hydrogenation of the alcohol in an acetic acid solution with platinum oxide the α -norborneol is obtained which is described in Annalen der Chemie, Vol. 512, 172 (1934). Fraction III rep-

resents the addition product of 2 mols of cyclopentadiene and 1 mol of vinyl acetate. The said compound corresponds to the following constitution:



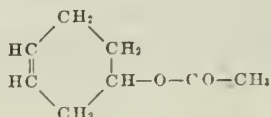
By saponification with methylalcoholic potassium hydroxide there is obtained therefrom the corresponding unsaturated alcohol of melting point 83°, which yields with phenylazide a hydrotriazole of melting point 194–195°.

Example 2

When replacing in the preceding example the 150 parts of vinyl acetate by 100 parts of vinyl formate and working under the same conditions, the formates of the two alcohols are obtained in form of colorless oils of boiling point 75–80° (at 20 mm pressure) or 140–143° (at 20 mm pressure) respectively.

Example 3

When heating equal parts by volume of butadiene-1,3 and vinyl acetate with the addition of polymerization inhibitors for 12 hours in an autoclave and distilling off the reaction mixture in vacuo, there is obtained besides some unchanged vinyl acetate and dimeric butadiene the addition product of the components, i. e. the Δ^3 -cyclohexane-ol-1-acetate in form of a colorless oil of boiling point 173–175° which corresponds to the following formula:



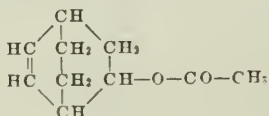
This compound, if subjected to catalytic hydrogenation takes up the amount of hydrogen corresponding to one double linkage, cyclohexanol acetate being formed thereby. By saponification with alcoholic potassium hydroxide the cyclohexanol of boiling point 155–156° is obtained therefrom, the phenyl urethane of this alcohol showing a melting point of 82°.

Example 4

When replacing in example 3 the butadiene by 2,3-dimethyl butadiene and working up in the usual manner there is obtained the 3,4-dimethyl- Δ^3 -cyclohexene-ol-1-acetate in form of a colorless oil of an intensively ester-like smell which on saponification with methylalcoholic potassium hydroxide is converted into the corresponding alcohol (phenyl urethane of melting point 112°C).

Example 5

By the addition of $\Delta^{1,3}$ -cyclohexadiene and vinyl acetate there is obtained, when working according to the preceding examples, the bicyclic acetate of the following constitution:

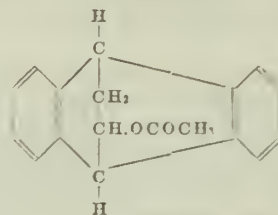


urated alcohol (phenylurethane of melting point 125–126°) by saponification with methylalcoholic potassium hydroxide.

Example 6

10 parts of anthracene in 120 parts of xylene are heated in an autoclave for 18 hours to 220–230° with the addition of 20 parts of vinyl acetate. The reaction being complete, the solvent and the excess vinyl acetate are evaporated, whereby the residue partly crystallizes; on sucking off and rinsing with methanol the precipitate proves to be identical with unchanged anthracene (1 part).

After a short time the methanol containing mother liquor forms a mass of crystals which represent the addition product of the components. On dissolving from alcohol colorless crystals of melting point 101°C are obtained which probably correspond to the following constitution:



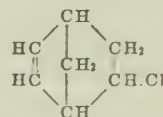
On saponification the ester yields the corresponding alcohol of melting point 142°.

Example 7

80 parts of vinyl chloride and 80 parts of cyclopentadiene are heated in an autoclave for 15 hours to 170–180°. On distilling off the unchanged vinyl chloride the residue is fractionated in vacuo. At 11 mm pressure the following two fractions are obtained:

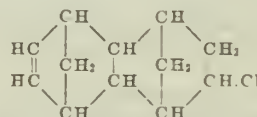
	Parts
I: 46–47°	73
II: 129–131°	28

Fraction I represents the chloride of the following constitution:



The hydrotriazol which is obtained therefrom by the addition of phenylazide melts at 115–116°.

Fraction II represents the addition product of 2 mols cyclopentadiene and 1 mol of vinyl chloride of the following constitution:



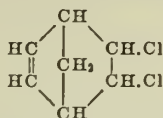
With phenylazide a hydrotriazol of melting point 195° is obtained.

Example 8

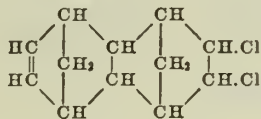
By a 15 hour's heating of 175 parts of 1,2-dichloroethylene with 125 parts of cyclopentadiene in an autoclave and after distilling off the reaction product in vacuo at 11 mm pressure as described in example 7, there are obtained the

which is converted into the corresponding unsat-

following two addition products of 1 or 2 mol of cyclopentadiene and 1,2-dichloroethylene:



of boiling point 74–76° at 11 mm pressure; the hydrotriazol shows the melting point 148°; and

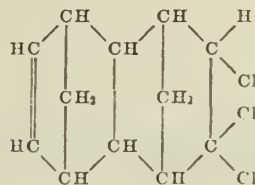


of boiling point 146–148° at 11 mm pressure; the hydrotriazol shows the melting point 210°.

Example 9

When adding trichloro-ethylene to cyclopentadiene while heating the components in an auto-

clave at 175–185° the addition product of 2 mols of the latter and the trichloroethylene of the following constitution is obtained:



This compound represents colorless oil which boils in vacuo at 11 mm pressure at 158–160°. With phenylazide it yields a hydrotriazole of melting point 225–226°.

KURT ALDER.
HANS-FERDINAND RICKERT.

ALIEN PROPERTY CUSTODIAN

WETTING, DISPERSING AND WASHING AGENT

Elsa Maria Jablonski, née Hofmann, Frankfurt-
Main, and Max Fischer, Offenbach A. M., Ger-
many; vested in the Alien Property Custodian

No Drawing. Application filed January 4, 1939

The present invention relates to the production and the use of a wetting, dispersion and washing agent which is obtained by the condensation of a carboxyl compound e. g. a carboxylic acid or its ester with a boric compound e. g. boric acid or boric anhydride and a polyvalent alcohol and subsequent sulphonation. The product may be employed as a wetting, dispersion, reviving and washing agent in the textile industry, and also in the paper and leather industry and in the cosmetic industry, this both in the form of the free sulphonic acid and also in the form of its neutral salt.

It is certainly known that valuable products are obtained by the esterification of carboxylic acids with polyvalent alcohols and subsequent sulphonation. These products, however, are resistant towards acids and alkalis to a restricted extent only, since they are split up again into carboxylic acids upon heating. Moreover, they are affected by concentrated alkalis. It has now been found that, by the condensation of carboxylic acids or their esters with polyvalent alcohols with the use also of boric acid or boric anhydride, products of an entirely different kind are obtained which, unexpectedly, are much more resistant towards acids and, in particular, towards alkalis.

In accordance with the invention, the new products may be produced in the following fashion:

One molecule of a carboxylic acid or one molecule of a carboxylic-acid ester is heated with two molecules of a polyvalent alcohol and one half molecule of boric acid H_3BO_3 or one half molecule of boric anhydride. In some cases, heating may be performed under pressure and at correspondingly higher temperature, or in vacuo at a correspondingly lower temperature, or in the presence of an inert gas. In some circumstances, it is more advantageous to carry out this process in the presence of a high-boiling solvent. It is then quite immaterial whether the boric acid is first brought into reaction with the polyvalent alcohol or whether a mixture of the three components all together is heated. The volatile substances formed in this reaction, such as water, excess polyvalent alcohol and decomposition products are distilled off.

The condensation product may be used by itself as a softening agent in the textile and leather industry. It may further be employed as a foam-preventing agent.

Particularly valuable are the sulphonation products of these new condensation substances and the salts produced therefrom. The neutral

products have soap-like properties without exhibiting the disadvantages of such soaps. They are soluble in water in completely neutral fashion, are not affected by sulphuric acid up to 6° Bé, and give no separation with concentrated common-salt or Epsom-salt solution. They are extremely resistant towards the hardness-producing substances in water, remaining perfectly clear even with water of over 100° DH. In conjunction with soaps, they prevent the formation of lime soaps to a certain extent. Precipitated lime soaps are dispersed by the products in accordance with the invention, so that the lime soaps are brought into a form in which they can be readily washed away. Even salt solutions of the heavy metals have no effect upon the new sulphonated products. Unexpectedly, however, the products are also very resistant towards alkaline substances without being subject at the same time to saponification. Clear solutions are obtained which remain clear, with the addition of up to 5% of phenol even with concentrations of up to 50° Bé of potash lye without turbidity or separation taking place after days. Consequently, these new products are particularly suitable for mercerisation and discharge printing. They are, moreover, also good emulsifying agents which are capable of converting comparatively large quantities of fatty acids, neutral fats, liquid and solid hydrocarbons and other substances insoluble in water into a water-soluble form, for which reason they can also be employed in the metal industry for the production of boring, grinding, and cooling agents. The new products are also suitable for the production of cosmetic and pharmaceutical products. Due to their good wetting powers, they are suitable, in combination with insecticide agents, for the extermination of vermin and vegetable pests.

The saturated and unsaturated fatty acids, their esters or their natural neutral oils are suitable as the carboxylic acids, also the resinic acids and their mixtures with fatty acids such, for example, as tall oil, further the naphthene acids, wool-fat acids and their natural wax-like cholesterides.

Glycol, di-glycols and polyglycols, glycerine and polyglycerines, erythritol, penta-erythritol, mannitol, sorbitol and the varieties of sugar are suitable as the polyvalent alcohols.

Concentrated commercial sulphuric acid and the maintenance of sulphonation temperature of less than 40°C suffice for the sulphonation. However, with appropriate precautions, sulphonation may also be performed with monohydrate, oleum

or chloro-sulphonic acid. In some cases, also, sulphonation may be effected in the presence of solvents which, as desired, may be left or distilled off. The sulphonation products may be neutralised with alkaline lyes, alkali carbonates, ammonia or organic bases such as triethylamine, triethanolamine, ethylenediamine or pyridine. Preferably the excess sulphuric acid is first washed out. However, it is then possible also to separate the acid sulphonation product from the washing water by suitable solvents such, for example, as hydrocarbons and then to neutralise and, in some cases, to distil off the solvent. Particularly concentrated products up to 60% content (calculated with reference to the content of condensation product) are obtained in this fashion. The final product may be produced in liquid form, in jelly-like and paste form with or without Glauber's salt. However, it is also possible to obtain a product, containing Glauber's salt, in powder form. The new product may be worked into soaps to which it imparts an increased resistance to lime.

No certain information can be given as to the chemical constitution of the new products. By comparatively detailed investigation, it has been determined that, for example, upon the condensation of ricinoleic acid with glycerine and boric acid, simple glycerine-monoricinoleate is not formed, but a product which contains two molecules of glycerine and one half molecule of boric acid to one molecule of ricinoleic acid. If the condensation product is washed with hot water a product is obtained which consists of one molecule of ricinoleic acid, one and a half molecules of glycerine and one sixth of a molecule of boric acid. The boric-acid content is maintained even after the sulphonation. If, in this condensation reaction, the boric acid is omitted, then the known glycerine-monoricinoleate is obtained which, after the sulphonation, does not exhibit the favourable properties like the condensation product obtained with the employment of boric acid. In a further experiment, distillation flasks respectively containing one molecule of stearic acid and two molecules of glycerine were set in the same heating bath. One half molecule of boric acid was added to one of the distillation flasks. Both preparations were heated to 340°C and thereafter washed with hot water. From the experiment with the boric acid, a product was obtained having 72.03% of stearic acid and 2.9% of boric acid. From the experiment without boric acid, a product having a 79.23% content of stearic acid was obtained.

Example 1

A mixture consisting of 298 parts of anhydrous ricinoleic acid, 184 parts of anhydrous glycerine and 31 parts of boric acid is heated in a distillation apparatus. The boric acid disappears between 120 and 130°C and two sharply separated layers are formed. A homogeneous clear liquid is obtained upon further heating up to 310°C. Approximately 51 parts of water, 47 parts of excess glycerine and 8 parts of an oily decompo-

sition product are distilled off. The yield amounts to 407 parts, or 79% of the originating material. The cool oil is stirred gradually in a suitable apparatus at between 30–35°C with 450 parts of concentrated sulphuric acid until a sample is clearly soluble in water. After 2–3 hours further stirring, 1200 parts of the ice water are added and the excess sulphuric acid is washed out therewith. After the removal of approximately 950 parts of acid water, there remain approximately 1100 parts of the sulphonated product. These are neutralised with approximately 310 parts by weight of soda lye of 40° Bé, 360 parts of Glauber's salt solution separating out again. 1050 parts of neutral product are obtained with a content of 28.8% of organic substance and 0.93% of boric acid.

The completely neutral product is suitable as a wetting agent in the dyeing industry and a solution of 3°/00 at 18°C gives a wetting period of 4 seconds, whereas 12 seconds was determined in a similar experiment with 50% Turkey-red oil. Moreover, the product, due to its softening and dispersive properties in the various finishing processes, is suitable also as a washing agent for artificial silk, cellulose wool, cotton, wool and coloured fabrics. It may be employed, as required, in acid, neutral or alkaline dye-baths. Due to its fat content, it imparts a soft feel to the goods. In combination with fat solvents or alcohols, the product may be employed as a cleaning or purifying agent or a conditioning agent, since it is weakly hygroscopic.

Example 2

141 parts of olein, 62 parts of glycol and 15.5 parts of boric acid are heated to 215°C, carbon dioxide being passed through. 23 parts of water, 4 parts of glycol and 8 parts of oil are thereby distilled off. The yield amounts to 178 parts. The product is sulphonated and worked up as in Example 1. A bright yellow oil is formed which is particularly suitable as a washing agent due to its dense and stable foam.

Example 3

A mixture of 142 parts of stearic acid, 92 parts of glycerine and 15.5 parts of boric acid are heated in vacuo at 16 mm. pressure to 240°C. 28 parts of water, 3 parts of glycerine and 3.5 parts of fatty acid are thereby distilled off. The yield amounts to 215 parts. The product is dissolved in 400 parts of carbon tetrachloride, sulphonated with 200 parts of 100% sulphuric acid and thereafter washed with 500 parts of ice water. The sulphonation product remains dissolved in the carbon tetrachloride and, after the separation of the acid water, is neutralised with 81 parts of triethanolamine. A bright yellow solution is obtained which completely emulsifies in water. The product may advantageously be employed as a spot-cleaning agent.

ELSA MARIA JABLONSKI,
NÉE HOFMANN.
MAX FISCHER.

ALIEN PROPERTY CUSTODIAN

METHOD FOR PRODUCING UNSATURATED CHLORINATED HYDROCARBONS CON- TAINING FOUR CARBON ATOMS

Walter Bauer, Darmstadt, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed January 9, 1939

In my patent applications Serial No. 212,823 and Serial No. 221,264 there are described methods for polymerizing chlorinated ethylenes such as dichlor ethylene and trichlor ethylene, the main product of the polymerization being a dimeric product such as dimeric dichlor ethylene having the formula $C_4H_4Cl_4$ and dimeric trichlor ethylene having the formula $C_4H_2Cl_6$. It has been found that such chlorinated ethylenes which are compounds containing four carbon atoms and at least four chloride atoms in their molecules and which can be prepared according to the method described in the above cited applications or by other methods e. g. by application of pressure and high temperatures to the said chlorinated ethylenes, may be converted to technically valuable unsaturated chlorinated hydrocarbons containing four carbon atoms in their molecule by splitting off a molecule containing chlorine i. e. either hydrogen chloride or chlorine.

The splitting off may be carried out by methods known per se, so the hydrogen chloride may be splitted off by an alkaline substance or by catalysts, and the chlorine may be splitted off by application of metals.

The products which are obtained by the described processes of splitting off hydrogen chloride or chlorine are proposed to be chlorinated derivatives of butadiene. They may be used high boiling solvents and/or softening agents, insecticides, insulating materials for electrical purposes etc. They are almost non-combustible, the more the higher the chlorine contents are.

The new compounds may be converted to resin-like compounds for use as plastic materials by treating them with aluminium chloride or similar catalysts. The new artificial resins which are obtained in form of powder may be used for moulded articles e. g. sheets or plates by the application of pressure and heat to the powder.

The new resins show a high molecular weight and are probably polymers of the starting materials.

Instead of the pure compounds with four carbon atoms, mixtures of two or more of the said compounds or mixtures of the said compounds with other substances especially unsaturated substances may be treated with aluminium chloride or similar catalysts according to the invention.

The reaction which yields substances of high molecular weight may be carried out in the presence or absence of solvents and/or diluents. The reaction occurs very easily if the starting materials have a low percentage of chlorine, e. g. $C_4H_4Cl_2$ reacts below room temperatures. The

reaction of substances showing higher chlorine percentage is preferably carried out by using higher temperatures.

Instead of aluminium chloride the addition products of aluminium chloride with other salts may be used e. g. with sodium chloride, lithia chloride or aluminium bromide and similar catalysts.

It was surprising that aluminium chloride and similar catalysts are suited for the production of high-molecular substances, since high temperatures, oxygen and peroxides alone or combination which each other have proved to be unsuitable.

The high molecular substances obtained are almost non-combustible and show a high insulating power, e. g. for electrical purposes. They may be combined with other artificial matter as for instance condensation products from formaldehyde and phenol or urea and the like, polymeric vinyl, acrylic or methacrylic compounds or the like, e. g. polymeric vinyl acetate, vinyl chloride, vinyl ethers, vinyl carbazole, vinyl acetylene, styrene, butadiene, monochlorbutadiene, acrylic and methacrylic acid and especially their esters and nitriles, furthermore with esters and ethers of cellulose, waxes, natural resins such as rosin, fillers, pigments, dyestuffs, softening agents. The additional substances may be used alone or in any desired combination. The high molecular substances obtained according to the invention are preferably mixed with low molecular, liquid starting products, especially with polymerizable substances. The polymeric chlorinated butadiens which are obtained according to the invention are for instance moistened with liquid monomeric esters of acrylic acid and polymerized to a rubber-like, non-sticky mass.

Examples

1. 250 g zinc dust are suspended by stirring in 250 ccm methyl alcohol and 500g dimeric dichlor ethylene are added within an hour. The temperature of the solution is raised to 70-75°C. In order to complete the reaction the whole may be heated to 75-80°C for some time. Two layers are obtained. The upper layer which is clear is separated and fractionated at 15 mm pressure. A yield of 70-80% of a chlorinated hydrocarbon showing a constant boiling point, is obtained.

The boiling point is 30-35°C at 15 mm pressure, $d_{20} = 1.214$; $n_D^{20} = 1.523$. The chlorine percentage was found to be 57.82 (calculated 57.72 for $C_4H_4Cl_2$).

Whereas the dimeric dichlor ethylene does not

accept any bromine, the reaction product obtained by splitting off one molecule of chlorine is capable of accepting two molecules of bromine. The reaction seems to show that the new compound is a dichlor butadiene. The product is not the same as the one known 1,2-dichlorbutadiene.

Instead of zinc, iron may be used for splitting off the chlorine but zinc is preferred.

2. 300 g dimeric dichlor ethylene are cooled to 0°C and while stirring the calculated amount of potassium hydroxide dissolved in methyl alcohol is added with-in 3 hours. The formed potassium chloride is filtered off, the two layers are separated and fractionated at 15 mm pressure. A pure chlorinated hydrocarbon boiling at 52–53°C is obtained in a yield of 85% of the theoretical. $d_{20}=1,382$; $n_D^{20}=1,546$. The chlorine percentage was found to be 67,43 (calculated 67,02 for $C_4H_3Cl_3$). Bromine is added in a similar manner as to the product according to example 1.

3. 80 g zinc dust are suspended by stirring in 50 ccm methyl alcohol and 150 g dimeric trichlor ethylene are added at 70°C within an hour. A temperature of 70–80°C is then maintained for another hour, continuously stirring. The upper of the two layers formed is fractionated at 15 mm pressure. The product which is obtained in a yield of about 70%, shows a boiling point of 64–67°C at 15 mm pressure, the formula is $C_4H_2Cl_4$.

4. The compound $C_4H_4Cl_2$ obtained according to example 1 is polymerized in the following manner. 3 g of dry aluminum chloride are added to 50 ccm ethylene chloride. While stirring and maintaining a temperature of about 0°C, 50 g of the chlorinated hydrocarbon are added with in half an hour. The stirring is continued at 0°C for 3 hours. The formed pappy black product is washed twice with hydrochloric acid and then twice with pure water. The pap was filtered off and a bluish product in the form of a powder was obtained in a yield of about 95%. Plates or similar molded articles may be prepared by pressing

the powder at about 70–90° C under high pressure.

5. 30 g of the new compound obtained according to example 1 are cooled down to 0–5° C. While maintaining the low temperature and stirring 1 g of dry aluminum chloride is added. The reaction begins after 5–10 minutes and is complete after about 30 minutes. The products are washed with diluted hydrochloric acid and then with wather. The blackish raw product became light yellow by the washing process. It was filtered off and dried at 50–60° C. The light coloured powdery product was obtained in a good yield. Molded articles could be obtained by pressing as described in example 4.

6. The powder obtained according to example 4 or 5 was mixed with its own weight of monomeric ethyl acrylate and the mixture was kept at room temperature until the powder is swelled to some extent. The mass was then heated to 50° C for 24 hours adding some benzoyl peroxyde. The temperature is raised to 70° C left for 24 hours. The monomeric ethylacrylate yields the polymeric product and tough practically not sticky mixtures are obtained.

7. 50 g of the new compound obtained according to example 2 are heated to 50–70° C and while stirring 3 g dry aluminum chloride is added. The reaction begins after a short time and is practically complete after half an hour. The black tough product is washed with methyl alcohol and worked up according to example 4. The yield is about 95%.

8. 30 g of the new compound obtained according to example 3 are heated to 50° C and while stirring 2 g dry aluminum chloride is added. The temperature is then raised to 70° C. Reaction occurs immediately. The product was worked up according to example 4. The yield was about 95%.

Instead of 2 g aluminum chloride 3 g aluminum bromid may be used.

WALTER BAUER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PRODUCING STYRENE

Martin Mugdan, Munich-Grosshesselohe, and
Johann Sixt, Burghausen, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed January 19, 1939

This invention relates to a process for the synthesis of styrene from benzene and acetylene.

It is known that styrene is formed when a mixture of benzene and acetylene is heated to high temperatures (Berthelot 1867, Liebig's Annalen 142, 259). This method has not been proved applicable for the technical production of styrene because the largest part of acetylene reacts in another undesired way. For the verification of Berthelot's method a mixture of 75 g. of benzene and 20 liters of acetylene was passed per hour with equal speed at a temperature of 600° C. through a tube of 20 mm diameter heated at a length of 600 mm which consisted of a chromium-iron alloy rich in chromium (Sicronal 12" of the firm Vereinigte Stahlwerke A. G., Düsseldorf). After two hours' trial the tube had been filled up with sooty coal. Only 2 g. of styrene were formed beside a larger amount of substances boiling at a temperature of above 130° C. An experiment on the same conditions but at a temperature of 800° C. yielded 3,6 g. of styrene. 35 g. of high-boiling substances were formed besides. In the tube 16 g. of coal were found. The waste gas did not contain any acetylene left. In applying a tube of quartz instead of chromium-iron the results were similarly unfavorable.

It has now been found that the heating of a mixture of acetylene and benzene in the vapour phase takes a surprising favorable course if the heating is performed at diminished pressure instead of an ordinary one.

Example 1

Per hour a mixture of 90 g. of benzene and 20 l of acetylene (measured at a pressure of 760 mm) was passed at a temperature of 900-950° C. through the above named tube of chromium-iron alloy. The tube and the conjuncted arrangement for condensation were brought by a pump to a pressure of 40 mm. The vapours after hav-

ing passed the heated tube entered a water cooled condenser and receiver. This condenser was connected with two low cooled receivers into which benzene condensed containing still some styrene. After two hours all the condensates were fractionally distilled. 9,5 g. of styrene were obtained. 6 g. (mostly diphenyl) distilled at a temperature of above 180° C. The tube contained only few soot. The unchanged benzene was regained practically quantitative. The waste gas contained 85% of acetylene beside hydrogen formed partly by the by-reaction of the formation of diphenyl. This gas may be used again in circulation or it may be used for another purpose.

On the same conditions of working but without using diminished pressure the tube choked already after a quarter of an hour by coaly separation.

Example 2

The apparatus was the same as in Example 1. At a pressure of 18-32 mm, a mixture of 45 g. of benzene and 20 l of acetylene (measured at ordinary pressure) was passed per hour through a tube heated at a temperature of 950-1000° C. After two hours 8,5 g. of styrene and 4,5 g. of high-boiling substances were obtained. The tube contained very few soot. A gas of 80% of acetylene was regained. By further diminishing the pressure the formation of by-products could be reduced further-more.

Example 3

Through the same apparatus a mixture of 45 g. of benzene and 5,5 l acetylene (760 mm) was passed per hour at a temperature of 900-950° C. and a pressure of 11 mm. In two hours 3,6 g. of styrene and only 0,7 g. of high-boiling substances were obtained. The gas was 80-90% of acetylene.

MARTIN MUGDAN.
JOHANN SIXT.

THE HISTORY OF THE
CITY OF BOSTON

FROM THE FIRST SETTLEMENT TO THE PRESENT TIME

BY SAMUEL JOHNSON

IN TWO VOLUMES

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ALIEN PROPERTY CUSTODIAN

THERMOPLASTIC MATERIAL AND A PROCESS FOR THE MANUFACTURE OF SAME

Asbjörn Aasen, Oslo, Norway; vested in the
Alien Property Custodian

Application filed January 27, 1939

No Drawing. Application filed January 27, 1939

The present invention relates to a thermoplastic material and process for the manufacture of same, which by heat treatment under pressure in moulds may be hardened to shaped objects, such as buttons, door-handles and the like.

It is previously known to produce artificial thermoplastic materials for similar purposes by condensation of phenols, thio urea, casein etc. with aldehydes, preferably formaldehyde.

It has now been found that a thermoplastic material may be obtained by treating the meat of fishes at elevated temperatures with an aqueous solution of an aldehyde, preferably formaldehyde. The fish meat is used in raw or dried form, preferably as fish meal. It is believed that it is the protein in the fish meat which reacts with the aldehyde to form the new product. However, also the skin and the bones of fish may be treated simultaneously. In such case these ingredients serve as fillers.

Example 1

Dried fish meal is mixed with water to a slurry. 25 cc. of a 40% formaldehyde solution per kg. fish meal (calculated on dry weight) is added

and the mixture heated. The reaction starts at about 70 degrees centigrade and according as the temperature rises the grains become heavier and settle on the bottom. After a treatment of about 6 hours at 100 degrees centigrade a workable thermoplastic material is obtained.

By further increasing the excess of the 40% formaldehyde solution used the heat treatment at 100° may be reduced to a quarter of an hour.

The finished thermoplastic material is filtered off and dried.

Example 2

Less water than in Example 1 is used, the fish meal being mixed with 250 cc. water and 25 cc. of a 40% formaldehyde solution per kg. fish meal which is heated under pressure at 110° for a quarter of an hour. A plastic mass is obtained which, after having been dried in the air during several days, results in a suitable thermoplastic material.

The invention also comprises moulded products obtained by hardening the thermoplastic material in moulds at temperatures from 150 to about 200° C.

ASBJÖRN AASEN.

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ALIEN PROPERTY CUSTODIAN

METHOD AND APPARATUS FOR PRODUCING UREA

Claus Koeppe, Oberhausen-Osterfeld, Germany;
vested in the Alien Property Custodian

Application filed January 30, 1939

It is known that urea ($\text{CO}(\text{NH}_2)_2$) may be produced synthetically by treating carbonic ammonia salts in autoclaves under pressure and at temperatures of about 150°C , the ammonia salts being charged into the autoclave either in solid or molten form. The ammonia salts forming the charging material for the urea synthesis may be produced in several ways, for instance, by vaporising under pressure a solution containing a high percentage of carbonate of ammonia



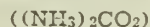
or carbamate of ammonia ($(\text{NH}_3)_2\text{CO}_2$), the resulting vapour-mixture, which consists of ammonia (NH_3), carbonic acid (CO_2) and some water, being passed into coolers in which the salts are precipitated either in the form of solids or as a molten mass. In order to produce urea the molten carbamate is then transferred to the urea autoclaves for further treatment. Now, it has been discovered that this commonly practised and comparatively expensive production of the highly saturated solutions of carbonic ammonia salts, which have to be prepared separately from pure charging materials, may be avoided by using in their stead ordinary strong ammonia liquor, such as produced in coke oven plants, gas works or low-temperature carbonising plants, as starting solution. Strong ammonia liquor is a raw product obtained in coke oven plants, gas works, low-temperature carbonising plants etc. by condensing the vapours produced in distilling diluted gas washing liquids or the condensates of crude gases. In addition to about 20–25% ammonia (NH_3), which is its chief constituent, the strong ammonia liquor contains many impurities, such as carbonic acid (CO_2), hydrogen sulphide (H_2S), heavy and light hydrocarbon compounds, cyanogen (CN), sulphocyanogen (CNS), phenoles and their homologues etc.

Now, the invention consists in making this raw and impure strong ammonia liquor of varying composition usable as an advantageous charging material for the commercial urea synthesis without any considerable preliminary purification by adapting the known process for the production of urea to the impurities and the varying composition of the strong liquor.

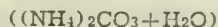
The production of strong ammonia liquor is commonly preceded by the removal of acid from the weak liquor which is to be treated to produce strong liquor. For this purpose the weak liquor is heated to about 90 to 95°C in so-called deacidifiers and most of the carbonic acid and hydrogen sulphide contained in the weak liquor is thus removed, direct steam being added if necessary. Owing to the preliminary removal of acid from the weak liquor higher percentages of ammonia are attainable in the strong liquor. According to the invention the acid is incompletely

removed from the strong ammonia liquor for the urea synthesis, i. e. the removal of acid is stopped prematurely, preferably after most of the hydrogen sulphide and a small part of the carbonic acid have been removed. Instead of operating with a reduced deacidification period the acid can also be removed from the weak liquor at low temperatures. The most favourable operating temperature for this incomplete removal of the acid is about 70 to 90°C , preferably $80^\circ \text{C} \pm 5^\circ$, according to the composition of the weak liquor and the quantity and nature of the steam which is introduced. The purpose of the incomplete deacidification is to pass most of the carbonic acid into the strong liquor for binding the ammonia in the form of carbamate ($(\text{NH}_3)_2\text{CO}_2$) later on. It is advisable, however, to adjust the deacidification process in such a way as to obtain a deficiency of carbonic acid in relation to the quantity of carbonic acid which is stoichiometrically required for binding the ammonia.

The strong ammonia liquor thus obtained is fed into a pressure vessel or—for further continuous treatment—into a second still. As no stoichiometrically prepared solutions are available, but only impure weak liquor with varying carbonic acid, ammonia and hydrogen sulphide content, a method of operation which may be adapted to the varying content of absorbed gases and vapours is required for distilling the gases and vapours from the strong liquor under pressure. In order to obtain as high a yield of urea as possible, however, the object of distilling the gases and vapours from the strong ammonia liquor under pressure must be to obtain a solid or—if the cooling is slight—a molten salt with a nitrogen content as high as possible in the coolers for precipitating the carbonic ammonia salts, these coolers being arranged in succession to the still. The production of carbamate



with as little carbonate of ammonia



and bicarbonate of ammonia ($(\text{NH}_4)\text{HCO}_3$) as possible is therefore aimed at. In order to obtain almost pure carbamate of ammonia ($(\text{NH}_3)_2\text{CO}_2$) strong ammonia liquor is, according to the invention, distilled under pressure, a surplus of ammonia being used in order to increase the partial pressure of the ammonia in the strong liquor to be charged and/or the pressure in the distilling apparatus being altered in accordance with the actual proportion of ammonia to carbonic acid, so that carbamate of ammonia is the only stable compound in the apparatus, being precipitated in the coolers from the vapours. In practice the pressures to be maintained in the distilling apparatus range

from about 10 atm. gauge when there is little carbonic acid present to about 30 to 35 atm. gauge when there is a large surplus of carbonic acid. In this way solid or molten salts with 90 to 95% carbamate of ammonia may without difficulty be continuously produced, superfluous carbonic acid as well as hydrogen sulphide (which has the highest vapour pressure), which may occasionally be present in the cooler, being simultaneously or separately blown off in a suitable manner. As ammonia may also escape in the removal of these gases the blown off gas is, according to the invention, furthermore returned to the crude gas current from the coke oven plant, gas works, low temperature carbonising plant etc. before it reaches the ammonia gas washers. Special washing devices arranged in succession to the distilling apparatus for recovering the ammonia may thus be dispensed with. All the above measures and operations are therefore not necessary in every case in order to obtain ammonia salts with a high carbamate content. The blowing off of the residual acids may therefore be dispensed with according to the nature of the strong liquor used, though its retention appears advisable owing to the fact that residual gases which are not combined with ammonia will slow down the formation of carbamate and consequently reduce the yield of the plant. Most of the impurities of the strong liquor mentioned at the beginning of this description remain in the water discharged from the strong liquor still. In addition the discharged water contains a residue of ammonia and carbonic acid, the quantities of which depend upon the equilibrium of absorption and the partial pressures of these gases and vapours in the presence of water at various temperatures and under different pressures. According to this invention this water discharged from the strong liquor still is returned to the weak liquor still, in which the residue of utilisable gases and vapours is removed.

The method according to the invention is further explained by the example of a plant shown in the diagram.

In this plant shown as an example the strong ammonia liquor is charged into the still *a* and the resulting gases or vapours passed into the coolers *b* arranged in succession to the still for precipitating or condensing the carbonic ammonia salts in solid or—if the cooling is slight—in molten form, the object being to obtain as high a nitrogen content as possible, i. e. the production of carbamate of ammonia ($(\text{NH}_3)_2\text{CO}_2$) with a minimum content of carbonate of ammonia ($(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}$) and bicarbonate of ammonia ($(\text{NH}_4)\text{HCO}_3$). Following its production the carbamate is transferred to the urea autoclave *c* in which urea is produced in the known manner. After the partial conversion of the carbamate ($(\text{NH}_3)_2\text{CO}_2$) into urea ($(\text{NH}_2)_2\text{CO}$) the salts of ammonia which are not converted are distilled over—also in the known manner—into a pressure vessel in which a lower temperature is maintained. Whereas special pressure-resisting receivers have been used up to the present for precipitating the resultant mixture of ammonia and carbonic acid gases and vapours in the form of ammonia carbamate, to which is added a large part of the hydrogen sulphide which enters the autoclave with the carbamate, it has been found that these residual gases and vapours are very much more easily and cheaply precipitated in the

coolers *b* arranged in succession to the strong liquor still for producing carbamate. In addition to the impurities carried along in the process, i. e. mainly sulphide of ammonium (NH_4SH), small quantities of hydrocarbon compounds and cyanogen compounds the urea solution leaving the autoclave *c* after having been thickened in the manner described above contains fresh impurities in the form of metallic sulphides, metallic oxides and thiourea ($(\text{NH}_2)_2\text{CS}$). Apart from these there are always also residual ammonia and residual carbonic acid in the watery urea solution. Whereas up to the present the residual gases and vapours separated from the urea solution were recovered in washers arranged in succession to the process, coke oven plants, gas works, low-temperature carbonising plants can, according to the invention, dispense with a separate secondary washer for waste vapours from the thickening pans *d*, which contain ammonia, carbonic acid and hydrogen sulphide by returning these waste vapours to the crude gas stream before it reaches the ammonia washers. It has further been found that the above-mentioned solid impurities, with the exception of the thiourea, may be removed almost completely from the watery urea solution by diluting the watery urea solution before it is thickened in the pan or pans *d* with a large quantity of water and then thickening it. As the diluted solution boils longer during the thickening the oxidiferous and sulphurated impurities assume a flaky form. In a diluted solution these flakes settle better than in viscous urea solutions and are accordingly more easily filtered. In addition they practically retain the whole of the hydrocarbon residues which are often present on the filter *e*. According to the invention it is advisable to thicken the urea solution (or melt) leaving the urea autoclave *c* in two stages by filtering off the impurities, which are converted into an easily filterable state by boiling up the diluted urea solution, after the last traces of ammonia and carbonic acid have been distilled off. This also ensures a saving in the oxidising agents to be added in the next operation.

The final operation consists of removing, according to the invention, the small quantities of thiourea contained in the solution by oxidation in the pan *f*. Dioxide of manganese (MnO_2), hydrogen peroxide (H_2O_2) and other known oxides are particularly suitable as oxidising agents. Hydrogen peroxide (H_2O_2) has the advantage of being free from residue. Moreover, by the addition of the oxidising agent any residual quantities of metallic oxides and metallic sulphides are, if necessary, converted into a very easily filterable form, so that a second filtration through filter *g* leaves a light and clear urea solution, which merely requires thickening to produce pure urea. The urea solution is thickened in the crystallising pan *h*, from which the urea is passed to a centrifuge *i*. The residual liquid discharged from the centrifuge *i* is returned to the crystallising pan *h* in order to recover the remaining particles of urea which are discharged in this water.

t is the collecting container for strong liquor, *p* the pump for strong liquor and *w* the preheater for preheating the strong liquor. The preheaters *w* and the pans *d* and *f* may be heated by heat exchange by utilising the waste heat of the process.

CLAUS KOEPEL.

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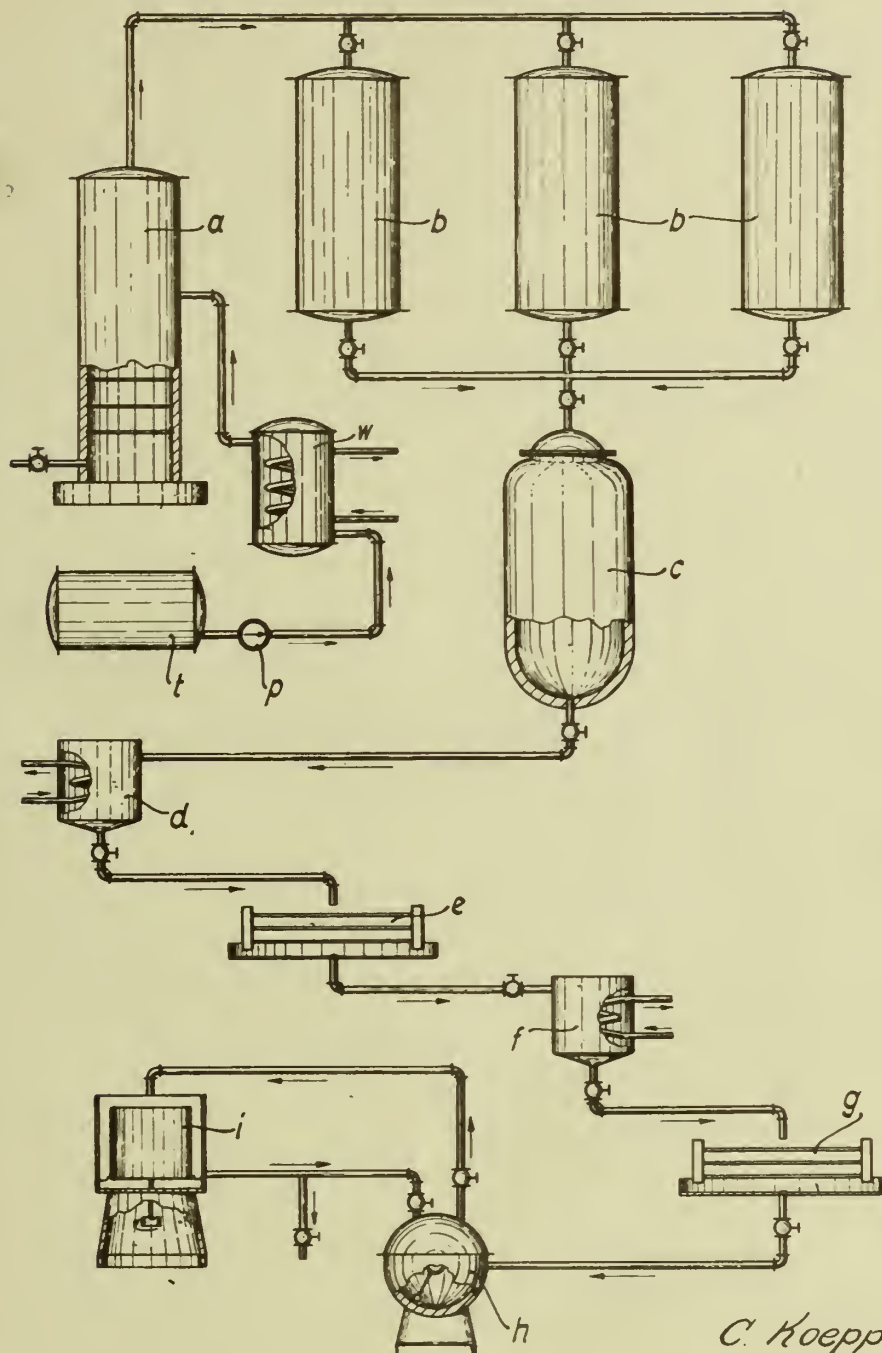
APRIL 20, 1943.

METHOD AND APPARATUS FOR PRODUCING UREA

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BY A. P. C.

Filed Jan. 30, 1939



C. Koeppe1
Inventor

By: Glascock Downing & Seebold
Atty.

ALIEN PROPERTY CUSTODIAN

STIMULANTS SUITABLE FOR COMBATING SYMPTOMS OF FATIGUE AND PROCESS FOR THEIR PRODUCTION

Felix Haffner, Tubingen, and Fritz Sommer, Berlin-Charlottenburg, Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 11, 1939

This invention relates to new stimulants suitable for combating symptoms of fatigue. The new stimulants contain as active principle aliphatic hydrocarbons having at least 4 carbon atoms and substituted at two adjoining non-terminal carbon atoms by one phenyl group and one amino or alkyl amino group or the salts of such substituted hydrocarbons.

The stimulants according to this invention thus belong, by their chemical constitution, to the group of aliphatic amines substituted by an aromatic radical. Numerous physiologically active substances occurring in nature belong to this large group of compounds. Among the earliest investigated were the physiological effects of compounds of the adrenaline type. These compounds are characterized by their capacity for peripheral stimulation of the sympathetic system.

Whilst in adrenaline the phenyl radical contains two adjacent hydroxyl groups, ephedrine possesses an unsubstituted phenyl radical. The stimulants provided according to the present invention also possess an unsubstituted phenyl radical. Ephedrine differs from adrenaline in that it exhibits stronger central effects which are manifested in an activation of respiration and increase of blood pressure. Ephedrine is an amino-alcohol and thus, like adrenaline, contains a hydroxyl group in the aliphatic side-chain. More recently, the physiological effects of an aliphatic amine substituted by a phenyl radical and free from hydroxyl groups, namely 1-phenyl-2-aminopropane, have been exhaustively investigated. 1-phenyl-2-aminopropane is distinguished from ephedrine by its still more prominently exhibited central effects; this is especially manifested in the influence of 1-phenyl-2-aminopropane on the psychical functions. For this reason 1-phenyl-2-aminopropane is suitable for combating fatigue conditions, for the relief of depressions and for combating conditions of intoxication.

The stimulants according to the invention, which contain as active principle aliphatic hydrocarbons having at least 4 carbon atoms and substituted at two adjoining non-terminal carbon atoms by one phenyl and one amino or alkyl amino group, are similar in action to 1-phenyl-2-aminopropane. The alkyl groups at the nitrogen atom may be methyl, ethyl, and propyl radicals. One as well as both the hydrogen atoms can be substituted by the abovementioned alkyl groups.

Of special importance among the new stimulants are those which contain 2-phenyl-3-aminobutane as active principle; besides these, stimulants which contain 3-phenyl-4-aminopentane as

active principle are also of practical importance, although to a somewhat lesser degree. 2-phenyl-3-methylaminobutane also has proved very active.

In comparison with 1-phenyl-2-aminopropane, 2-phenyl-3-aminobutane is distinguished by its very much milder action. Whilst the quantities required to produce the first observable effects are about equally large for the two compounds, and amount in experiments on animals to about 0.01 mg. per gram weight of the animal, the toxic dose with the previously known 1-phenyl-2-aminopropane is about ten times the amount of the minimum dose, whilst with 2-phenyl-3-aminobutane only 20 times the amount of the minimum dose has a toxic action. The increase of the quotient toxic dose: effective dose is a great advantage of the new stimulants. The action of the new stimulants which contain 2-phenyl-3-aminobutane takes place as rapidly as that of the previously known stimulants containing 1-phenyl-2-aminopropane. An especial advantage of the new stimulants containing 2-phenyl-3-aminobutane is however the fact that their action ceases more rapidly than that of stimulants which contain 1-phenyl-2-aminopropane. This more rapid cessation is of especial importance in relation to the fact that it is frequently necessary to combat symptoms of fatigue for a short time only, whereas after the expiration of the period during which wakefulness is desired a normal sleep is required. The shorter period of action of the new stimulants containing 2-phenyl-3-aminobutane as active principle is not detrimental, inasmuch as when a longer period of wakefulness is desired this can at any time be attained by means of a renewed dose.

Owing to their milder action, as described, the new stimulants are principally of importance for combating symptoms of fatigue in normal persons. The practical importance of a stimulant suitable for combating symptoms of fatigue in normal persons is very great. For example, numerous motor accidents when driving at night are due to the driver falling asleep. This danger can effectively be combated by means of the new stimulants. The new stimulants are further of value to persons who suffer from great tiredness at certain times of the day. Such conditions of lassitude are frequently combined with coincident psychical depressions. The new stimulants prove advantageous in all these cases. Since for the most part it will be a matter of a frequently recurring use of the stimulants, it is a great advantage that they show no undesirable secondary affects. For example, the stimulants containing

2-phenyl-3-aminobutane or 2-phenyl-3-methylaminobutane as active principle do not even produce the unpleasant feeling of dryness in the mouth which frequently arises as a consequence of the action of 1-phenyl-2-aminopropane. Further, no habituation to the new stimulants is developed, so that continually increasing doses are not rendered necessary; in addition, no craving for the new stimulants is to be observed.

Another field of application for the new stimulants is the combating of symptoms such as appear after the use of narcotics and hypnotics, for example the combating of the effects of alcoholic intoxication and of the symptoms of poisoning after excessive doses of barbituric acid derivatives. Owing to the milder action of stimulants containing 2-phenyl-3-aminobutane as active principle, larger doses are required in these cases than would be with stimulants containing 1-phenyl-2-aminopropane as active principle. Owing to the smaller toxicity of 2-phenyl-3-aminobutane, this fact is however of no importance and the new stimulants are as suitable for these purposes as are the stimulants containing 1-phenyl-2-aminopropane as active principle.

As has already been described, the stimulants according to the invention which are of the greatest importance are those containing 2-phenyl-3-aminobutane or 2-phenyl-3-methylaminobutane as active principle. Besides these, the stimulants containing 3-phenyl-4-aminopentane as active principle are also of importance. In comparison with 1-phenyl-2-aminopropane these stimulants however show not only a milder, but also a definitely weaker action, whereas it is an especial advantage of the stimulants containing 2-phenyl-3-aminobutane, again in comparison with 1-phenyl-2-aminopropane, that their action with regard to the combating of symptoms of fatigue in normal persons is not weaker but only milder, i. e., of shorter duration and not accompanied by secondary effects.

The new stimulants may of course be used in combination with other medicines. They may, for example, be used instead of caffeine in mixtures containing a stimulant such as caffeine. The combined use with other stimulants, such as stimulants of the uric acid series, e. g., caffeine, is however also envisaged, whereby superadditive effects are sometimes to be observed. Finally advantageous results also result from the combination of the new stimulants with ephedrine.

The new stimulants, whose active principle is an aliphatic hydrocarbon having at least 4 carbon atoms and substituted at two adjoining non-terminal carbon atoms by one phenyl group and one amino or an alkylated amino group, may contain the given compounds either as such or in the form of their salts. The salts of all acids which do not for their part bring about undesirable physiological effects may be used. As inorganic acids there may be mentioned, for example, hydrochloric acid, sulfuric acid, phosphoric acid; as organic acids, acetic acid, lactic acid, tartaric acid may be named.

The most varied methods of application of the new stimulants may be employed. A very prompt action is produced on oral application of the new stimulants. For oral application, the salts of the new compounds will mainly be used. These salts may be manufactured into tablets, dragées or similar products. Since doses of 5 to 10 mg. are mostly concerned, the tablets are very small. Owing to their good solubility, an

extensive resorption of the stimulants takes place already in the oral cavity. An especially rapid action is thereby produced. Since the salts of the new stimulants have a good solubility in water, the preparation of aqueous solutions which may be applied in drop form also comes into consideration. The sulfuric acid salt of 2-phenyl-3-aminobutane is soluble up to 14% in water, so that relatively concentrated solutions may be prepared, whereas the limit of solubility of 1-phenyl-2-aminopropane sulfate is about 7%.

For percutaneous application of the new stimulants, solutions in salves, suppositories or other oily or fatty solvents are of especial importance. For the preparation of these solutions in oily or fatty solvents, either the bases themselves or suitable salts such as, for example, the oleic acid or fatty acid salts of the given compounds may be used. Finally the inhalation of the new stimulants may also come into consideration, whereby preparation containing the free base may appropriately be employed, or aqueous solutions of the salts of the active compounds may be finely divided in a spraying apparatus and the air thus charged may be inhaled.

For purposes of injection, aqueous solutions of the salts of the new compounds are of primary importance. The same is true for cases where the new compounds are to be applied in the form of eye-drops.

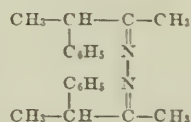
The new compounds contain at least two centres of asymmetry, these being

(1) the carbon atom to which the phenyl group is attached, and

(2) the carbon atom to which the amino group is attached.

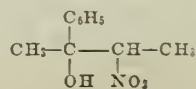
Owing to the non-equivalence of these two centres of asymmetry, the new compounds must exist in the form of two pairs of optical antipodes not agreeing in their physical properties and two racemates. These stereoisomers all display the described physiological effects, although perhaps in different degrees.

The preparation of the new stimulants is carried out according to the usual organic chemical methods for the synthesis of amines. One mode of preparation consists in the conversion of the corresponding ketone into the oxime and the reduction of the oxime to the amino compound. As an example there may be given the reaction of 2-phenyl-3-butanone with hydroxylamine and the reduction of the oxime so obtained to 2-phenyl-3-aminobutane. The same amine is obtained if 2-phenyl-3-butanone is converted by means of hydrazine into the azine:

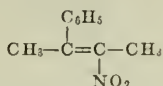


which by reduction and splitting of the N—N linkage likewise yields 2-phenyl-3-aminobutane.

Another process with not such good yields consists in the reaction of acetophenone, or its homologues in which the methyl group is replaced by a higher alkyl radical, with nitroethane. A nitro-alcohol is hereby first formed, for example

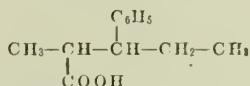


which is converted by dehydration into the corresponding nitroethylene



By reduction of this nitroethylene, 2-phenyl-3-aminobutane is again obtained.

A method of preparation which has proved particularly satisfactory likewise starts with a ketone, but a purely aliphatic ketone, for example methyl ethyl or methyl propyl ketone. This is converted by means of sodium bisulfite into the corresponding sodium bisulfite addition compound. By reaction of the bisulfite compound with potassium cyanide the corresponding cyanhydrin is obtained, which gives on hydrolysis an α -hydroxy-carboxylic acid. By dehydration of this α -hydroxy-carboxylic acid, an acrylic acid alkylated at both the carbon atoms connected by the double bond is obtained. With the aid of aluminium chloride, benzene can be added on to this compound so that a hydrocinnamic acid is obtained, for example when methyl propyl ketone is used as the initial material there is obtained



The carboxyl group may then be converted into an amino group by known methods, for example by decomposition according to Hofmann or Curtius. An especially elegant conversion of the carboxyl group into the amino group consists, according to F. Schmidt, in the reaction of the acid with hydrazic acid in the presence of a suitable catalyst, for example concentrated sulfuric acid. In the case of the use of methyl propyl ketone as initial material, there is obtained in this manner 3-phenyl-4-aminopentane. In the preparation of the N-alkylated amines, the above described primary bases are employed as initial materials and subjected to the customary alkylating methods. For example, the primary amines may be converted, by means of p-toluenesulfonylchloride, into the toluenesulfonamides which, as sodium compounds, may then be reacted with alkyl halogenides. By boiling with acids, under pressure if desired, the toluenesulfonyl radical can then be split off whereupon the secondary bases are obtained which in turn can be converted, by means of inorganic or organic acids, into the corresponding salts.

The invention is illustrated but not limited by the following examples.

EXAMPLE 1

Preparation of 2-phenyl-3-aminobutane

520 grams of sodium bisulfite solution (33-40°Bé) are added with cooling and continuous agitation to 144 grams of methyl ethyl ketone. The reaction mixture sets after a few minutes to a solid mass and is allowed to cool completely when a solution of 130 grams of potassium cyanide in 200 c. c. of water is added; the bisulfite crystals thereby dissolve and the cyanhydrin separates as a colorless oil. Crude yield 203 grams.

The cyanhydrin is hydrolised, either with 4 times its volume of concentrated hydrochloric acid or with twice its weight of 96% sulfuric acid,

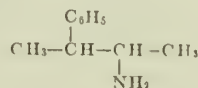
to form methyl ethyl glycolic acid. 195 grams of pure methyl ethyl glycolic acid having a melting point of 71-72°C are obtained (83% of the theoretical yield, calculated on the methyl ethyl ketone).

358 grams of methyl ethyl glycolic acid and 450 grams of acetic anhydride are heated together for 4 hours on an oil bath at 150°C. The acetic acid is subsequently distilled off. 250 grams of dimethyl acrylic acid are isolated from the distillation residue (84% of the theoretical yield).

30 grams of dimethylacrylic acid (dissolved in 220 grams of thiophene-free, dry benzene) and 100 grams of finely powdered anhydrous aluminium chloride are allowed to stand for 1 week at 40-45°C. Ice and concentrated hydrochloric acid are added to the reaction mixture. The benzene and aqueous layers are thereafter separated and, after evaporation of the benzene, 30 grams (56% of theoretical yield) of an acid boiling at 129-132°C. can be isolated from the residue by vacuum distillation at 5 mm. pressure. After one recrystallization from petroleum ether and benzene the melting point is 132°C.

Analysis gave a carbon content of 74.3% and a hydrogen content of 7.95%. For α,β -dimethyl hydrocinnamic acid the carbon content is calculated to be 74.2 and the hydrogen content 7.88%.

25 grams of this α,β -dimethyl hydrocinnamic acid are dissolved in 100 c. c. of chloroform. 50 c. c. of concentrated sulfuric acid are added as a layer below the solution and 16 gm. of sodium azide are added in portions to the reaction mixture slowly enough for the temperature of the reaction mixture to remain at 40-45°C. This temperature is maintained for a further 4½ hours until the evolution of gas has stopped. The reaction mixture is then poured on to ice, and by addition of alkali and extraction with ether 14.9 grams (71% of the theoretical yield) of 2-phenyl-3-amino-butane.



with a boiling point of 87-90° C at 13-14 mm. pressure, or with a boiling point of 72° C at 8 mm. pressure, may be isolated from the aqueous phase.

The α,β -dimethyl hydrocinnamic acid serving as an intermediate product in the preparation of 2-phenyl-3-aminobutane may be obtained by another method. A method of preparation of α,β -dimethyl hydrocinnamic acid which proves satisfactory is as follows:

630 grams of acetophenone (b. p. 202°C) are boiled with 905 grams of pure α -bromopropionic acid ethyl ester in 800 grams of benzene with 350 grams of zinc wool for 4 hours. The reaction product is decomposed by means of dilute sulfuric acid and the benzene solution is distilled in vacuo. The α,β -dimethyl phenyl hydracrylic acid ethyl ester so obtained distils over at 140-142°C under 12 mm. of mercury. The main fraction amounts to 780-890 grams, which corresponds to 70-80% of the theoretical yield.

To dehydrate this compound, 800 grams of the ester in 3 litres of benzene are boiled with 200 c. c. of phosphorus oxychloride for one hour. The reaction product is decomposed by means of ice and the benzene phase is distilled in vacuo. α,β -dimethyl cinnamic acid ethyl ester, which boils at 140-146°C under 22 mm. of mercury, is obtained

in a yield which is 65-70% of the theoretical amount.

To hydrolyse this ester, 500 grams of the ester are boiled with 1.5 kgs. of 36° Bé caustic potash until a clear solution is obtained. After acidification, the solution is extracted with ether. The residue from the ether solution solidifies to a crystalline mass; β -dimethyl cinnamic acid having a melting point of 111-112°C is obtained in 80% yield.

The β -dimethylcinnamic acid is hydrogenated by dissolving the acid in an equivalent amount of alkali and then hydrogenating it with colloidal palladium according to Paal and Skita. α,β -dimethyl hydrocinnamic acid, which can be recrystallized from 85% formic acid, and then melts at 133°C., is obtained in good yield by this method.

α -methyl hydrocinnamic acid substituted in the β -position by a higher alkyl radical in lieu of a methyl group can be obtained if the next higher homologues are used in place of acetophenone as starting material in the reactions described above. Propiophenone is consequently to be used as starting material for the preparation of α -methyl- β -ethyl hydrocinnamic acid.

The conversion of the hydrocinnamic acid into the corresponding amino compound is carried out in all cases according to the known methods of Hofmann, Curtius or F. Schmidt for the replacement of a carboxyl group by an amino group.

EXAMPLE 2

Preparation of 3-phenyl-4-aminopentane

260 grams of methyl propyl ketone of boiling point 101-102.5° C. are added to 1050 grams of commercial sodium bisulfite solution of 38-40° Bé. A solid mass of the ketone bisulfite addition compound is formed on shaking. A solution of 260 grams of potassium cyanide in 400 c.c. of water is added to this mass with cooling and brisk shaking; an oil, methyl propyl cyanhydrin, thereby separates out. The yield is quantitative. The cyanhydrin is hydrolysed by boiling for 5 hours with 1600 c.c. of conc. HCl on a water-bath. By extraction with ether, drying the ethereal solution and evaporation of the ether, 290 grams of crude methyl propyl glycolic acid are obtained.

This crude product (290 grams) is boiled under reflux with 400 grams of acetic anhydride for 4¾ hours on an oil-bath. The reaction mixture is then distilled, using a fractionating column; 103 grams of a product with a boiling point of 202-212° C. (methyl ethyl acrylic acid) thereby distills over.

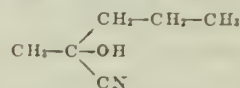
103 grams of this acid are allowed to stand together with 630 c.c. of dry benzene and 200 grams of finely powdered aluminium chloride for 3 weeks at 40-45° C. After the expiration of this time the reaction mixture is poured on to 1500 grams of ice and 600 grams of concentrated hydrochloric acid, the benzene layer is separated in a separating funnel and the aqueous layer is again shaken out with benzene. The benzene solutions are united, shaken with water, and dried with CaCl₂. After evaporation of the benzene, an oil remains. Weight 85.2 grams, boiling point 154-158° C at 5 mm. of mercury.

33 grams of this product, α -methyl- β -ethyl hydrocinnamic acid, are dissolved in 100 c.c. of chloroform, 75 c.c. of concentrated H₂SO₄ are added to form a layer below the solution and 20 grams of sodium azide are added, the temperature being constantly maintained at 45° C. After the evolution of gas has stopped, the reaction

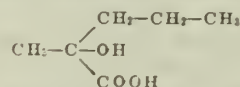
mixture is poured on to ice, separated from chloroform in a separating funnel, and again extracted with ether. The strongly acid aqueous phase is made strongly alkaline, and after extraction of this aqueous solution with ether, drying the ethereal solution with solid potassium hydroxide, and evaporation of the ether, 10.3 grams of an amine (37% yield) boiling at 75-76° C. at 5 mm. are obtained. The sequence of the reactions in this mode of preparation will appear from the following scheme:



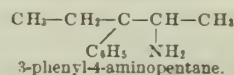
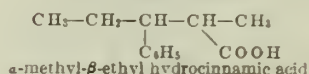
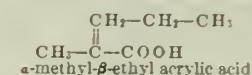
Methyl propyl ketone



Methyl propyl ketone cyanhydrin



Methyl propyl glycolic acid



EXAMPLE 3

Preparation of N-methyl-2-phenyl-3-aminobutane

To 14.9 grams of 2-phenyl-3-aminobutane suspended in 100 cc of 5 N-sodium hydroxide solution there were added while stirring 27 grams of toluenesulfonylchloride in portions. After a short time the reaction was finished whereupon the sulfonamide was extracted with ether. The ether residue was dissolved in 50 cc of alcohol and 50 cc of sodium hydroxide solution (20 per cent), and allowed to stand with 15 grams of methyl iodide for a few hours. The mixture was then slowly heated at 90° C. the alcohol being distilled off while the methyl compound precipitated. The latter was taken up in ether, the ether was evaporated, and the residue consisting of the toluenesulfonamide of the secondary base was heated with 50 per cent sulfuric acid at 140 to 150° C for 5 hours. After rendering the solution alkaline, the methylated base was driven off with steam, extracted with ether, and distilled. After a small quantity of first runnings, pure N-methyl-2-phenyl-3-aminobutane distilled at 103 to 104° C under 15 mm Hg.

In the production of the corresponding N-ethyl- or N-propyl-amine, ethyl or propyl iodide are used in a similar manner.

EXAMPLE 4

Preparation of 2-phenyl-3-aminobutane sulfate

In order to produce 2-phenyl-3-aminobutane sulfate (C₁₀H₁₅N)₂.H₂SO₄, 29.2 grams of base boiling at 96° C. under 15 mm were neutralized with 22.6 cc of N 8.58-sulfuric acid, and the mixture was concentrated in a desiccator. 37 grams of the neutral sulfate, m. p. 280° C., were obtained.

7 parts by weight of water, at 20° C., dissolve 1 part by weight of sulfate.

EXAMPLE 5

Preparation of acid 2-phenyl-3-aminobutane tartrate

20 grams of base were dissolved in 50 cc of methyl alcohol and admixed, while cooling, with

a solution of 20 grams of d-tartaric acid in 50 cc of water. Upon standing, the major part of the bitartrate crystallizes, while the rest can be obtained by concentrating the filtrate. Melting point 159 to 165° C.

FELIX HAFFNER.
FRITZ SOMMER.

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF NUCLEOSIDES

Hellmut Brederick, Leipzig, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed February 20, 1939

This invention relates to a process for the manufacture of nucleosides from nucleic acids. The invention is more particularly concerned with a process in which the nucleosides in nucleic acids are obtained by the action of bases on nucleic acids at an elevated temperature.

Attempts have already been made to isolate nucleosides from nucleic acids by means of ammonia at temperatures of 175–180°C in an autoclave, but the yields of the individual nucleosides which were obtained in this manner were only small. In particular the working up of the solution obtained by this process was an extremely laborious and complicated operation. Attempts to split up nucleic acids by means of alkali at temperatures below 175–180°C have hitherto always led to the production of nucleotides and not to the production of nucleosides. The production of nucleosides in a satisfactory manner by a chemical process has therefore not yet been accomplished.

On the other hand it is also known to obtain nucleosides from nucleic acids with relatively good yields by a fermentative hydrolysis. The disadvantage of a process of this nature lies mainly in the difficulty of producing a ferment suitable for the splitting up of the nucleic acids. Further, after the nucleic acid has been split up the ferment employed must again be removed from the solution by heating.

One object of the present invention is to obtain nucleosides from nucleic acids without it being necessary to make a special ferment and to effect the splitting up of the nucleic acid by purely chemical methods. A further object of the invention is to considerably shorten the time necessary for the hydrolysis of the nucleic acids as compared with the time necessary when the hydrolysis is effected with ferments. A still further object of the invention is to make it unnecessary to heat up the solution after the hydrolysis is complete for the purpose of removing the ferment.

As compared with the previously known purely chemical process of splitting up nucleic acids an object of the present invention is to considerably improve the yield of nucleosides and in particular to obtain approximately quantitative yields of nucleosides such as guanosin, adenisine, cytidine and uridine. Another object is to avoid, during the hydrolysis, any injury to the sensitive chemical compounds with which the present invention is concerned. In this connection a particular object of the invention is to obtain the

nucleosides in a practically pure state and preferably directly in a crystalline form.

A still further object of the invention is to reduce the temperature necessary for the chemical hydrolysis of the nucleic acids so that the use of an autoclave can, in general, be dispensed with. Finally, yet another object of the invention is to simplify and cheapen the process of obtaining nucleosides from nucleic acids by recovering from the solution which is treated by the process of the invention the base which is employed for splitting up the nucleic acid and using it again for splitting up the next batch of fresh nucleic acid.

These and other objects of the invention are realised by splitting up nucleic acids in an alkaline medium at a temperature lying below 175–180°C and continuing the hydrolysis for a longer period than in the known processes which have only led to the separation of nucleotides. I have found that, by working in this manner, nucleic acids split up without trouble into nucleosides. Thus, for example, if nucleic acid is boiled under a reflux cooler in an alkaline solution, that is to say for example with an addition of caustic soda or potash solution or baryta water, or if the solution is merely heated on the water bath, the nucleic acid is split up with the formation of nucleosides. By working up the solution obtained in this manner I have succeeded in obtaining the nucleosides. It is true that the separation of the nucleosides from the solution obtained presents some difficulty because alkali phosphate is produced during the hydrolysis which sometimes prevents the crystallisation of the guanosine in the solution from proceeding smoothly.

For this reason therefore I prefer a method of operation in which organic bases are employed as the agent for splitting up the nucleic acids. The use of volatile organic bases such as pyridine, quinoline, aniline and their homologues, analogues and derivatives has proved to be particularly advantageous. Instead of such organic bases I can also use aliphatic bases such as, for example, mono-methylamine, diethylamine, trimethylamine and their homologues or derivatives. Thus, for example if nucleic acids are boiled for some time in aqueous pyridine under a reflux cooler it is readily split up to form nucleosides. The duration of the splitting-up process depends mainly on the degree to which the phosphoric acid is split off from the nucleic acid. This splitting off of phosphoric acid can be easily determined analytically by methods which are known

to the chemist. As distinguished from alkalies, pyridine as well as other volatile bases can be separated by distillation. In this way the guanosine can be directly isolated in crystalline form. The filtrate from the guanosine can be treated directly with picric acid whereby adenosine picrate is obtained in a really pure state. The decomposition of the adenosine picrate and the recovery of the pure adenosine proceeds without trouble. For this purpose the process described in my prior German specification No. 650,847, is preferably employed. Adenosine can however be obtained directly as such in crystalline form from the filtrate from the guanosine after removing the phosphoric acid and any impurities by methods which are known to the chemist.

As will be clear from what has already been stated above, the new process is carried out at considerably lower temperatures and without the use of an autoclave. By this means destruction of the sensitive chemical compounds which are in question, and, in particular, the nucleic acids and the nucleosides is avoided. The yields obtained are consequently decidedly improved and guanosine and adenosine in particular are obtained with nearly quantitative yields. When an organic base is used as the agent for splitting up the nucleic acid the working up of the solution is enormously facilitated, since when the splitting up is effected, as described in the technical literature by means of ammonia, a gelatinous mass is obtained which must first be purified. Further, in the latter case the ammonium phosphate formed must be removed, otherwise when picric acid is added it would precipitate together with the adenosine picrate in the form of the difficultly soluble ammonium picrate.

As compared with the fermentative splitting up of the nucleic acids, the present invention not only has the advantage that the process is independent of the ferment and its manufacture but the duration of the hydrolysis is considerably shortened, the yields are also improved and a product of greater purity is obtained. In particular the adenosine picrate obtained by the process of the present invention is in general

purier than the picrate obtained when the splitting up is performed by fermentation.

The volatile base which is recovered by distillation from the solution produced by the process can be used again for the next batch of nucleic acid to be treated whereby the process is considerably simplified and the cost reduced. Owing to the adenosine being obtained in a pure crystallised state the process of obtaining the cytidine and uridine is improved and simplified.

The process will now be explained with the aid of the following example. The invention is in no way limited to the individual measures described in the example or to the exact sequence of operations as numerous modifications can be made which will be at once obvious to the technician.

Example

50 grams of yeast nucleic acid are boiled in 300 cc of aqueous pyridine under a reflux cooler until the phosphoric acid has been completely split off, that is to say for about 96 hours. After clarification with animal charcoal the solution is evaporated in vacuo. The residue is taken up in water and again evaporated. The guanosine which is insoluble after the addition of water is filtered off after cooling down in the ice chest. The yield is about 10 grams. The filtrate is treated with some NaOH for removal of the remains of pyridine and evaporated. The residue is taken up with water, the aqueous solution is heated slightly and treated with 25 grams of picric acid. After cooling in the ice chest the liquid is filtered off from the adenosine picrate which separates. The yield is about 18-22 grams. The pyrimidine nucleosides, cytidine and uridine, are obtained in known manner by working up the filtrate. To obtain the free adenosine directly, the filtrate from the guanosine is freed from phosphoric acid with baryta water and then from any impurities with lead acetate or with an organic solvent miscible with water. The adenosine crystallises out of the filtrate, which if necessary may be reduced. The filtrate can be worked up directly to cytidine and uridine.

HELLMUT BREDERECK.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PREPARING WATER-SOLUBLE CONDENSATION PRODUCTS

Hans Herbert Schiedewitz, Oschatz, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed March 10, 1939

It is already known from French Patent Specification No. 674,517 to treat fats, fatty acids or resins together with hydrocarbons or substitution products thereof, and in addition substances which contain the groups OH, COSH, COOH, CO, O, OC, CO, with chlorsulphonic acid.

According to the present invention sulphonated condensation products are made from esters of fatty acids, low molecular or high molecular, monobasic or polybasic, more particularly liquid esters, with monohydric alcohols, low-molecular and high-molecular, of aliphatic, aromatic or hydroaromatic nature, or phenols, naphthols or the like, together with polynuclear hydrocarbons, their hydrogenation products or derivatives such as naphthols, chlornaphthalene, naphthylamine. By simultaneous sulphonation and condensation the esters can be bound to the hydrocarbons with formation of true condensed sulphonic acids. Preferably operations are carried out by treating the mixture of hydrocarbon and ester with sulphonating agents such as oleum, chlorsulphonic acid, concentrated sulphuric acid, SO₃, in a stirring arrangement whilst thoroughly admixing.

The reaction may take place at elevated or reduced temperature; if the temperature is too high relatively dark products are obtained. Preferably operations are carried out with both reaction components present dissolved in one another or molten; both components also may be dissolved in a solvent. However, it is not absolutely necessary for both components to be dissolved in one another at the beginning of the reaction; but naphthalene, for example, if sulphonation is effected at relatively low temperature, may still be in the crystallised state at the commencement and may form a homogeneous mixture only as the reaction progresses. The reaction can be carried out at temperatures of 10-100° C. At relatively low temperatures of course preferably liquid hydrocarbons are taken, such as tetraline, or operations are carried out in the presence of solvents. At temperatures above 100° C dark products are obtained. The reaction may also be facilitated by adding condensing agents, such as phosphorus pentachloride, thionyl chloride, sulphuryl chloride, phosphorus oxychloride, during the addition of the sulphonating agent. In this way sulphonating agents are economised or better condensation is obtained more rapidly. As esters are used more particularly waxes, such as sperm oil, bottle-nosed whale blubber, or artificially prepared waxes. These artificially prepared waxes may for example be prepared by treating natural glycerides or waxes with low-

molecular alcohols in the hot under pressure in the presence of carbonic acid or sulphurous acid, when as a result the starting material is re-esterified in such a way that in place of the glycerin of the glycerides or of the alcohols of the wax the added low-molecular alcohol enters into the compound and forms an artificial ester. Large-surfaced bodies, such as active carbon, clay and so forth, as well as emulsifying agents may also be added in the conversion. However, the esters may also be prepared directly by uniting acids and alcohols in the hot under pressure in the presence of the gaseous acid anhydrides CO₂ or SO₂; here again large-surfaced substances may be added. Moreover the reaction water forming is removed as well. Useful products are also obtained with sperm wax or montan wax. Similarly, other esters of fatty acids and monohydric alcohols or phenols, as well as such as are made by the above-mentioned methods, may also be used. Also mixtures of different esters and mixtures of different hydrocarbons and mixtures of these mixtures may be used. As multi-ring hydrocarbons pre-eminently naphthalene, tetrahydronaphthalene and anthracene are used.

The products obtained are oils, pastes, or after evaporating down or spraying solid substances, according to the starting materials.

The sulphonic acids which form cannot be split even after boiling for days with concentrated acids or alkalies. They are stable towards the hardness formers of water. The products can be neutralised with organic or inorganic bases. The reaction products are used as outstanding washing, wetting, emulsifying and scrooping agents. Emphasis is to be laid on the softening action of the products. Further they show good emulsifying, dispersing and dye-dissolving action. The sulphonated condensation products have special importance for the softening and preparation of cellulose wool. They may however also be employed for treating other fibrous substances.

Example 1

90 parts of sperm oil and 35 parts of naphthalene are condensed with sulphonation at 40° C with 150 parts of 25% oleum in a stirring arrangement. The acid mass is allowed to stand over-night, washed next day with concentrated common salt solution and neutralised with concentrated soda lye. The reaction time amounts to three hours. Washing with concentrated common salt solution can also be omitted and in place thereof the sulphonate diluted with some water be directly neutralised. The product is ad-

justed to 33% sulphonate former, but may also be adjusted to any other sulphonate former content. The product serves for the purposes mentioned in the specification, especially as washing and softening agent.

Example 2

100 parts of 25% oleum are allowed to run slowly into a mixture of 100 parts of sperm oil and 50 parts of tetrahydronaphthalene at a temperature of 30° C whilst thoroughly stirring. After addition of the oleum 100 parts of chloresulphonic acid are added, likewise whilst stirring, at the same temperature, and on the next day, after washing with concentrated common salt solution, neutralisation is effected with triethanolamine. The reaction takes eight hours. The neutral product obtained dissolves readily in water and is absolutely stable to acid. The product may be used with advantage for preparing raw cellulose wool. It makes this loose and soft.

Example 3

50 parts of the phenyl ester of oleic acid and 50 parts of naphthalene are condensed with sulphonation with 200 parts of 25% oleum at about 50° C. The sulphonation takes about three hours. The sulphonate is allowed to stand overnight. The sulphonate is neutralised with soda lye either directly or after washing with common salt solution. The soda lye may be wholly or partly replaced by pyridine, triethanolamine or some other organic base. The product is adjusted to 33% sulphonate former.

Example 4

80 parts of naphthalene are sulphonated with 100 parts of 25% oleum. The naphthalene sulphononic acid is prepared at about 70° C. The temperature is then lowered and 120 parts of sperm oil at 40° C. are added and 150 parts of 25% oleum, likewise at 40° C. The product is neutralised after standing over-night and washed with com-

mon salt solution. The reaction time altogether amounts to about five hours. Adjustment is effected to 33% sulphonate former.

Example 5

90 parts of sperm oil and 35 parts of naphthalene are treated with 125 parts of oleum and 20 parts of phosphorus trichloride under the conditions of Example 1. The reaction time amounts to eight hours. The whole is allowed to stand over-night, washed and neutralised with soda lye and/or an organic base such as triethanolamine.

Example 6

100 parts of sperm oil and 50 parts of naphthalene are sulphonated at 100° C. with 100 parts of oleum. The oleum is added in the course of two hours. The reaction product is diluted with water and neutralised. A light brown paste is obtained. The acid sulphonate can of course also be washed and after neutralisation be adjusted to a definite sulphonate former content.

Example 7

90 parts of sperm oil and 35 parts of naphthalene are sulphonated at 35–40° C. with 125 parts of 25% oleum. During the sulphonation 20 parts of thionyl chloride are added. The reaction time amounts to about three hours. After the reaction is completed the whole is allowed to stand for some time, then washing is effected with common salt solution and neutralisation with soda lye, a part of the soda lye being replaced if desired by triethanolamine.

Example 8

100 parts of sperm oil and 25 parts of naphthalene are sulphonated at 30° C. with 150 parts of 25% oleum. The reaction time amounts to three hours. Washing is then effected with common salt solution, followed by neutralisation.

HANS HERBERT SCHIEDEWITZ.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF PLASTIC MATERIALS AND NEW INDUSTRIAL PRODUCTS RESULTING THEREFROM

André Henri Victor Durr, Paris, and Alfred André Issler, Creil, France; vested in the Alien Property Custodian

No Drawing. Application filed March 21, 1939

The gelatinisation of secondary cellulose acetate or diacetate takes place easily by malaxation with acetone in open receptacles. On the contrary it is not possible to gelatinise by this means the cellulose acetates of an acetyl content greater than 58%, commonly known as triacetates, and it is necessary in order to succeed in this to replace the acetone by a solvent of the triacetate. Now, the choice of such solvents is limited to toxic chlorinated solvents and to a few non-chlorinated and expensive solvents. It has however likewise been proposed to gelatinise the triacetates at temperatures of 150-190° C in cyclohexanone, benzyl acetate and so on, but this method has the inconvenience of necessitating the employment of large quantities of these solvents of high boiling point.

According to our present invention, we have disclosed that it is possible to prepare with ease plastic materials having a base of cellulose acetates of an acetyl content greater than 58% by treating the latter by a light or medium organic liquid capable of gelatinising them at a temperature above its boiling point under atmospheric pressure, this treatment taking place in a closed receptacle at a temperature above the boiling point of the organic liquid considered and therefore under pressure; then in transforming the gel obtained into a tenacious material according to customary processes.

The acetates of cellulose possessing an acetyl content greater than 58%, or triacetates, to which the invention is applicable are those which can be obtained by starting from natural cellulose, principally in accordance with the processes said to be in a dissolving or homogeneous medium and those said to be in a heterogeneous medium.

The words "light or medium organic liquids" are intended to indicate the organic liquids or mixtures of organic liquids having a boiling point lower than 150°C at atmospheric pressure. These liquids can be classed in three categories in view of their dissolving or gelatinising action in respect of the triacetates:

- a) those which are already solvents or gelatinisers of the triacetates at a temperature below their boiling point;
- b) those which are only solvents or gelatinisers at a temperature above their boiling point;
- c) those which even at a temperature above their boiling point have no solvent or gelatinising effect upon the triacetates.

It is necessary in order to carry out our invention to utilise an organic liquid belonging to

the first or second of these categories. With the liquids of the first category it is possible to gelatinise the triacetates without working under pressure, but recourse to this measure, in accordance with our invention, accelerates the gelatinisation. With the liquids of the second category only the application of the process of our invention permits of the gelatinisation.

As examples of liquids of the first category may be mentioned methylene chloride, mixtures of methylene chloride and lower alcohols, dioxane, mixtures of dioxane and acetone, mixtures of chloroform and lower alcohols.

As examples of liquids of the second category may be mentioned acetone, ethyl acetate, mixtures of acetone and ethyl acetate, of acetone and benzene, of benzene and methyl alcohol and the majority of the solvents of the diacetate.

As some of these examples show, the liquids of the first or the second category can be constituted by mixtures containing liquids belonging to the third category, that is to say having no solvent or gelatinising effect with respect to triacetates, or even by mixtures composed exclusively of liquids of the third category. It is in fact known that a mixture of non-solvent liquids for a given cellulose ester may constitute a solvent for the same ester. In the case of any liquid or mixture of liquids it is easy to determine by experiment to which of the three above categories it belongs and consequently whether it is applicable for carrying out the invention.

In order to carry out the invention it is possible to employ cellulose triacetate of fibrous nature in the form of flocks or in the form of blocks obtained by compression of flocks, which can bring its apparent density to 0.6 for example; these blocks moreover very easily break down in malaxation. According to the invention these flocks or blocks are mixed with the light or medium organic liquid and if desired with other solvents or gelatinisers, diluents, plasticisers, colouring materials, filling materials, other cellulose derivatives, synthetic resins and other ingredients employed in the manufacture of plastic materials. This mixture can advantageously be made in an autoclave with agitation or in a closed malaxator, or in any other appropriate apparatus. During the operation the apparatus is brought to a temperature above the boiling temperature under normal pressure of the most volatile of the liquids employed.

As plasticisers can be employed in particular the phenols substituted by at least one aliphatic or isocyclic chain having more than two atoms of

carbon, their halogenated derivatives or their derivatives substituted by the group OH. As examples of such plasticisers may be mentioned thymol, monochlorinated or dichlorinated para-tertiary butyl phenol, iso-octyl phenol, the cyclohexyl phenols and their hydroxy-ethyl, dihydroxy-propyl, acetyl and benzoyl derivatives. These products are obtained according to the general known methods by condensation of phenols with alcohols or olefines, followed if desired by halogenation and/or acylation or hydroxy-alkylation.

The gel of tri-acetate obtained according to the process described above is subsequently transformed into a tenacious material according to one of the customary processes for the transformation of gels. It is possible for example to laminate them in the hot or cold in order to obtain sheets which are stacked one on top of the other; the block thus obtained is subjected to pressure in the hot, then to cutting according to the customary practice in the manufacture of celluloid. It is also possible to transform the block into brittle leaves and to grind the latter in order to obtain a moulding powder which is converted into finished products by moulding under pressure. In the course of the laminating or grinding or at any other time in the manufacture it is possible to add to the mass filling materials, colouring materials and other ingredients.

The following examples illustrate the invention, without limiting the same thereto:

Example 1

	Parts
Cellulose tri-acetate, (acetyl content 61,5) ..	100
Acetone	200
Chlorinated butyl phenol.....	100

are charged into an autoclave and malaxated for some hours at 110° C. The pressure rises to 5 kgs. The mass is converted into a homogeneous gel which, after cooling, can be laminated, then compressed and cut into thin sheets in accordance with practice analogous to that employed in the manufacture of celluloid. Furthermore, this gel can be converted into moulding powders according to customary practice.

When operation is conducted in an open receptacle the temperature is limited to the boiling temperature of the acetone and it is impossible to obtain a gel with the same charge.

Example 2

	Parts
Cellulose tri-acetate, (acetyl content 61,5) ..	100
Ethyl acetate.....	200
Chlorinated butyl phenol.....	50
Tri-acetin	25

are charged into a malaxator under pressure and heated to 120° C. for some hours. The pressure

rises to 3,500 kgs. A gel is obtained which, after cooling, can be treated by lamination as described in Example 1.

By operation without using pressure and even by working with a reflux condenser at the boiling point of the ethyl-acetate, it is impossible to obtain a gel under the conditions set forth.

Example 3

	Parts
Cellulose tri-acetate, (acetyl content 61,5) ..	100
Acetone	60
Benzene	96
Methyl alcohol.....	44
Chlorinated o-phenyl-phenol.....	100

are heated for some hours under pressure at 120° C and the gel obtained is worked as described in Examples 1 and 2.

By operating with the same charge but without using pressure it is possible to obtain gelling of the cellulose acetate.

Example 4

The method of working described in the preceding examples is applied to a mixture constituted by:

	Parts
Cellulose tri-acetate, (acetyl content 61,5) ..	100
Benzene	100
Acetone	100
Chlorinated butyl phenol.....	100

The triacetate can be employed in the form of blocks previously compressed in a press, which increases the apparent density to 0.6.

Without working in an autoclave it is impossible to obtain a gel under the conditions set forth.

Example 5

	Parts
Cellulose tri-acetate, (acetyl content 61,5) ..	100
Benzene	100
Methyl alcohol.....	110
Chlorinated butyl phenol.....	100

are malaxated for some hours under pressure at 120° C and the gel obtained is treated as described in examples 1 and 2.

Example 6

	Parts
Primary cellulose acetate having an acetyl content 58.5.....	100
Ethyl-toluene-sulphamide	16
Tri-acetine	34
Acetone	150

are charged in an autoclave and malaxated for eight hours at 80° C. The mass becomes transformed into an homogeneous gel which is treated as described in Examples 1 and 2.

ANDRÉ HENRI VICTOR DURR.
ALFRED ANDRÉ ISSLER.

ALIEN PROPERTY CUSTODIAN

HIGHER MOLECULAR SUBSTANCES FROM ALLYL CHLORIDE AND ITS HOMOLOGUES

Walter Bauer, Darmstadt, and Franz Götz, Darmstadt-Eberstadt, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 10, 1939

The invention relates to the production of higher molecular substances from allyl chloride and its homologues.

It has been found that allyl chloride and its homologues may be converted into technically valuable, higher molecular substances by the action of peroxide catalysts such as benzoyl peroxide, acetyl peroxide, ethylene peroxide, and tetralin peroxide. The conversion is preferably carried out at somewhat elevated temperature. In order to secure a satisfactory conversion, when ordinary pressure is used, (that is, at temperatures up to the boiling point of the raw material) a reaction period of at least several days is necessary. The reaction period may also be shortened by operating under increased pressure and elevated temperature.

The higher molecular compounds obtained vary according to the nature of the raw materials employed. In general, a plurality of higher molecular compounds are obtained simultaneously from a single raw material. A portion of the raw material remains unaltered in every case. It may be recovered by distillation and again subjected to the converting process.

The allyl chloride and its homologues may also be subjected to the treatment of the invention while mixed together with each other or with similarly reacting compounds, e. g. s-dichloroethylene or trichloroethylene, and with chlorine-containing ethylene derivatives in general which are not per se capable of being polymerized to high molecular artificial products. The mixing may be effected either prior to or during the conversion. In these cases, higher molecular compounds will also be formed to a certain extent, which contain a number of the raw materials as their constituents. In addition to or in lieu of such compounds, it is also possible to add other substances, e. g. solvents, dispersing agents, softeners, fillers, resins, rubber, cellulose, and compounds of such substances, either prior to, during, or after the conversion.

The 2-methyl allyl chloride may with special advantage be subjected either alone or mixed with other substances to the action of the peroxide catalysts.

The products produced in accordance with the present invention are apparently mixtures of lower and higher polymers. For example, when 2-methyl allyl chloride is converted, the dimeric products predominate; allyl chloride predominately yields a higher molecular product.

Example 1

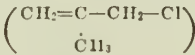
100 parts by weight of allyl chloride are boiled in reflux fashion with 1% benzoyl peroxide for 4 weeks. Fractionation of the reaction product yields the following:

	Parts by weight (unaltered allyl chloride)
at 46-54°	56
54-63°	8
112-150°/14 mm	1.4
150-254°/14 mm	3.5
Distillation residue:	30.4

The residue is a viscous, sticky, non-combustible mass which is applicable as a softening agent, adhesive, lubricant, for preparing lacquers, and for impregnating purposes.

Example 2

1500 g. of 2-methyl allyl chloride



are boiled in reflux fashion with 1% benzoyl peroxide for 8 days. Fractionation of the reaction product yields:

at 68- 78°	940 g.=62.7%	unaltered 2-methyl allyl chloride
80- 92°	476 g.=32.4%	dimeric 2-methyl allylchloride
135-140°/12 mm.	5.1 g.=.34%	
140-180°/12 mm.	15 g.=1.0%	
180-200°/12 mm.	14.5 g.=.97%	
200-240°/12 mm.	21.8 g.=1.45%	
Distillation residue:	12.4 g.=.83%	

The principal product of the reaction, the dimeric 2-methyl allyl chloride, after purification, exhibits a boiling point of 84.5 to 85° at 13 mm., a specific gravity of .9328 at 20°, and a refractive index n_D^{20} =1.477. Under normal pressure the product boils at 194-196° and decomposes. The molecular weight was found to be 177 (the theoretical is 181).

The dimeric 2-methyl allyl chloride is colorless and water-clear and has an agreeable, terpene-like odor. It is difficultly inflammable and exhibits no tendency to split off hydrochloric acid spontaneously. It is insoluble in water but miscible with most organic solvents. It may be used as a detergent, insecticide, and also as a solvent and diluent, since it has a good solvent capacity e. g. for most artificial and natural resins.

WALTER BAUER.
FRANZ GÖTZ.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF DI-AMIDE AND POLYAMIDE RESINS

Ignaz Kreidl, London, S. W. 1, England, and
Franz Nozicka, Vienna, 19, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed April 17, 1939

This invention relates to a process for the production of di-amide or polyamide resins. Di-amide and polyamide resins are known. They are usually produced by condensation of di-amides or polyamides with aldehydes, especially formaldehyde, the condensation being either acid, alkaline or neutral. The invention is based on the knowledge, that di-amide or polyamide resins with new properties can be obtained by converting aromatic disulfamides or polysulfamides or aromatic dicarbamides or polycarbamides and also those di-amides or polyamides which contain at least one sulfamide group and one carbamide group, into methylol compounds while avoiding polymerisation and that the methylol compounds thus formed can be treated with substances which can separate formaldehyde from the methylol compound, preferably in at least such quantity, that from every two molecules of the methylol compound while separating at least one mol formaldehyde a new compound is formed, preferably a compound with at least one methylol group, preferably with two methylol groups, but if the separation of formaldehyde is continued, or allowed to go too far, the product obtained by the separation is condensed with formaldehyde with the result that one or several methylol groups can again be introduced into the compound, so that the required compound is formed. In the process according to the invention the separation of formaldehyde can be carried so far that the compound of the desired composition is only obtained by a condensation with formaldehyde following the separation of formaldehyde.

If for example disulfamides are to be produced, it is preferable to use a dilution which is obtained by using a 1/2% formaldehyde solution.

The process according to the invention leads to resins which are absolutely insoluble in water.

Therefore, in the process for the production of resins according to the invention, di-amides or polyamides are first converted into methylol compounds, for example in a known manner by condensation of the di-amides or polyamides with aldehydes, particularly formaldehyde, a polymerisation of this methylol compound being, however, prevented at the same time, so that substantially monomeric methylol compounds are formed.

The methylol compounds thus produced are, according to the invention, treated with substances which are capable of separating formaldehyde from the methylol compound, that is with such substances in at least such quantity that from two molecules of the methylol compound one molecule of a new compound is formed, with

separation of at least one mol of formaldehyde, particularly a compound with at least one methylol group but preferably a compound with two methylol groups.

5 However, the separation can be carried farther and the product thus obtained can be condensed with formaldehyde in such a manner that the compound of the desired composition is produced.

10 The methylol compound is preferably treated with ammonia or a substance giving off ammonia for the separation of the formaldehyde, it being possible to use ammonia in aqueous solution or in gaseous form.

15 Thus, for example, to two molecules of a dimethylol compound the equivalent in ammonia for one mol formaldehyde that is 2/3rd mol ammonia to two mols of the dimethylol compound, is added. If started, for example, from a toluol disulfamide dimethylol, about 11 kilogrammes of 20 100% ammonia (NH₃) are added to 600 kilogrammes of this compound. An increase in the ammonia addition is detrimental on account of a saponification.

25 The resins produced according to the present invention are also suitable for the production of compositions for pressing but also as lacquers, spraying substances, protecting layers. The resins offer particular advantages in combination with other resins. In such a combination the resins according to the invention cause an increase in the flowing capacity and an increase in the resistance to water. Thus, these resins offer advantages in combination with carbamide resins, not only in rendering unnecessary the use of thio- 30 carbamide, but they are superior to thiocarbamide as addition to carbamide. Thus, an addition of about 10% of the quantity of thiocarbamide hitherto used for the production of carbamide-thiocarbamide-formaldehyde resins is sufficient to obtain resins which are equivalent to the carb- 35 amide-thiocarbamides.

40 In the production of such mixed resins, for example from carbamide formaldehyde resins and resins according to the invention, the effect of the ammonia or the like can be carried out in the sense of the invention also in any stage of the condensation process of the mixture.

Examples

50 1. Dissolve 4.5 kilogrammes of toluol sulfamide in 180 litres of water at about 70° C, and add about 100 grammes of soda and about 3 kilogrammes of 40% formaldehyde solution. After several hours the dimethylol compound separates out in the form of a chalky powder.

Triturate 6 kilogrammes of toluol disulfamide-dimethylol in about 30 litres of warm water and add slowly, while stirring 550 grammes concentrated ammonia solution, in stirring the while. A white fused mass separates out which mass is washed and dried. This condensation compound is dissolved in alcohol, if necessary with addition of suitable softeners.

The product thus obtained is very suitable as coating varnish, as protective coating for different photographic or graphic purposes and the like. The films are glass-clear and in every respect very resistant.

2. For the production of a carbamide mixed resin 18 kilogrammes of carbamide are dissolved in 18 kilogrammes of water. 1.8 kilogrammes of the condensation compound obtained for example according to Example 1, are dissolved in this solution under heating. This mixture is then condensed, formaldehyde, and if necessary condensing agents being added. The mixed resin obtained in this manner is converted in known

manner into a composition for pressing. This composition possesses, besides excellent flowing properties, a particularly great resistance against boiling water.

5 3. For the production of a carbamide mixed resin 18 kilogrammes of carbamide are dissolved in 18 kilogrammes of water. 1.8 kilogrammes of the toluol disulfamide-dimethylol obtained according to Example 1 are dissolved in this solution, under heating whereupon 150 grammes of concentrated ammonia solution are added and the whole is heated until the ammonia has disappeared. Then, after adding formaldehyde and, if necessary, condensing agents, the mixed resin is produced which in known manner is converted into plastic composition. This composition has the same excellent flowing properties and the same high water resistance as the composition obtained according to Example 2.

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IGNAZ KREIDL.
FRANZ NOZICKA.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF A BINDING AGENT FOR FIBROUS SUB- STANCES

Carl Ernst Willy Oesterreich, Berlin-Wilmers-
dorf, Germany; vested in the Alien Property
Custodian

No Drawing. Application filed May 3, 1939

The present invention relates to the produc-
tion of a binding agent, based upon sulphite waste
liquor, for fibre substances of all kinds. This
binding agent, because of its production and com-
position, is capable on the one hand of being
mixed in desired concentrations with water to
form a completely uniform stable emulsion and
on the other hand of being precipitated from this
emulsion by addition of suitable reagents and
binding firmly to fibrous substances of all kinds
in a finely divided disperse condition.

The technical, concentrated sulphite waste li-
quor from the sulphite cellulose process forms the
starting material for the production of this bind-
ing agent. It is known that sulphite waste li-
quor is a good emulsifier for various organic prod-
ucts such for example as asphalt, tar, pitches, res-
ins, oils, hydrocarbons etc. and that by its use
aqueous dispersions of these products can be pro-
duced. These dispersions however do not possess
the properties necessary for a good fibre binding
agent, because the products which may be pre-
cipitated therefrom by coagulation do not bind
adsorptively onto the fibrous substances, but after
coagulation has been effected by addition of suit-
able substances remain freely suspended in the
liquid containing the fibrous substance and upon
separation of this liquid from the fibrous sub-
stance are for the greatest part separated with
the liquid.

The employment of sulphite waste liquor as
starting material for the production of a binding
agent for fibrous substances would also have been
regarded as impracticable because it was known
that the sulphite waste liquor is very readily de-
composed by addition of coagulant substances
such as acids or acid salts, the ligno sulphonic
acid being precipitated with splitting off of free
acetic acid. Here however it is precisely the
organic complex, namely the lignosulphonic acid,
the preservation of which represents an essential
feature for the technical success of the binding
agent according to the invention, which is de-
stroyed.

It has now been found that it is possible in the
following manner to build up from sulphite waste
liquor a binding agent in which the sulphite waste
liquor is protected on the one hand from decom-
position by the action of the precipitating re-
agents and on the other hand is so closely com-
bined with the additional substances distributed
therein that upon precipitation of this binding
agent from its aqueous emulsion no separation
of the sulphite waste liquor from the additional
substances takes place. The substances con-

tained in the sulphite waste liquor, particularly
the lignosulphonic acid, remain on the contrary
in fixed chemical combination with the addition
substances precipitating and are precipitated to-
gether with the latter upon the fibrous substance
in finely disperse form. This effect is obtained
by the following treatment of the sulphite waste
liquor.

The technical, concentrated sulphite solution is
first mixed with albumen or albumen-containing
substances or solutions or emulsions thereof.
Products such as yeast, yeast-like substances,
milk, casein and the like come into consideration
as such albumen-containing substances. The ad-
dition of these substances effects the stabilisa-
tion of the sulphite waste liquor against the de-
composing action of precipitating agents.

Further, the sulphite waste liquor has added
to it an addition of aromatic amines, mono-, di-
or polyamines or derivatives thereof by way of
example aniline, phenylene diamine or the like.
These additional substances serve the purpose of
chemically binding the sulphite waste liquor com-
plex to the organic substances to be distributed
in it, and in this way it is ensured that these sub-
stances upon subsequent addition of precipitating
reagents are not precipitated by themselves, but
because of their linkage effected through the aro-
matic amines onto the sulphite waste liquor com-
plex the latter is precipitated in association with
them.

Organic substances, which together with the
sulphite waste liquor complex form the binding
agent according to the invention, are now intro-
duced by simple stirring and emulsifying, prefer-
ably with simultaneous moderate heating to
about 60°C, into the sulphite waste liquor pre-
pared in the above manner and containing the
albuminous substances and aromatic amines. As
such substances there preferably come into con-
sideration phenol-aldehyde resins in the resol con-
dition, heat-hardenable carbamide resins, bitu-
mens, drying oils, hydrogenated fatty alcohols or
fatty acids, phenols in the presence of aldehydes,
metal soaps of fatty acids or resins, tars, espe-
cially wood tar, asphalt, glue, casein or similar
protein substances etc. singly or in admixture
with one another. The choice of these addi-
tional substances or mixtures thereof as regards
composition and quantitative proportions de-
pends upon the particular requirements which
are to be made upon, and are to be fulfilled by,
the fibrous substance product produced with em-
ployment of the binding agent.

The binding agent is ready when the last men-

tioned additional substances have been introduced. It represents a thickly liquid, highly viscous, liquid mass which is more or less dark coloured according to the type of the additional substances and is indefinitely stable without decomposition and may be distributed in water to form an entirely homogeneous milk-like emulsion in any desired quantitative proportions, even at very high dilutions.

The precipitation of the binding agent upon dispersed fibrous substances of desired kind is undertaken in manner known per se as follows:

The binding agent according to the invention is added in desired quantity to a paste of fibrous substance dispersed in water. The said quantity may amount to a few per cent, calculated upon the solid fibrous substance; it can however be increased to higher percentages, to about 40% when the demands upon the finished product so require. After addition of the binding agent the paste of fibrous substance represents a milky liquid in which the fibres are distributed. The precipitation of the binding agent is effected by addition of acid reacting water-soluble substances. The addition of a mixture of equal parts of aluminium sulphate and zinc chloride is particularly suitable. However other acid reacting salts, inorganic acids in appropriately low concentrations, or organic acids such as lactic acid and the like may also be employed as precipitating agents.

Upon addition of these precipitating reagents, deposition of the binding agent milkily dispersed in water immediately takes place in finely distributed disperse form upon the surface of the fibres. It is characteristic and decisive for the technical value of the binding agent according to the invention that the entire complex of the binding agent, including the high molecular substances contained in the sulphite waste liquor, precipitates upon the fibres, so that the fibres loaded with the binding agent are now suspended in a clear watery liquid containing substantially only water-soluble low molecular components of the binding agent and the other additions.

The paste of fibrous substance loaded with the binding agent can now be brought into the paper machine and worked up to paper, board, and the like in the usual manner. The finished products thus produced show considerably better mechanical properties, in particular greatly improved tensile strength, compared to products produced with employment of the previously known binding agents.

It has further been found that products of outstanding excellence and quite unusual mechanical properties, in particular having strengths hitherto not attained in this field, can be produced in that the fibrous substance loaded with the binding agent, after removal of the aqueous liquid and forming into layers upon the paper machine, are dried and subjected to hot pressing in manner known per se. In this way shaped bodies may be produced of desired form, preferably plates, rods, tubes, beams etc. which as regards mechanical strength surpass the previously known pressed materials of fibrous substance and in many ways are suitable for replacing wood, especially plywood and similar improved products as well as many metals. The pressed bodies produced may on the one hand be treated, drilled, sawed etc. like wood and on the other hand are to a high degree indifferent chemically and physically.

The following examples illustrate how the invention may be carried into effect:

1. 1000 parts of concentrated sulphite cellulose waste liquor of about 30° Be are stirred with 100 parts of yeast or yeast-like products, which are dissolved in 100 parts water, and with 100 parts of aniline. The mixture is heated to about 60°C. and combined with stirring with 10% of its total weight of a phenoplastic resol or a carbamide resin or a mixture of these two. 150 parts of glutin (glue) are swelled and melted in 150 parts of water and 30 parts of a fatty alcohol mixture of 15 parts glycerine and 15 parts cetaceum are introduced into the melt. The mixture is carefully heated and emulsified with 30 parts of birch tar. Thereupon it is combined hot with the sulphite waste liquor mixture and stirred. The thickly liquid mass obtained is indefinitely stable and may be distributed in water in any proportion to form a homogeneous dispersion.

2. 500 parts of anhydrous sulphite cellulose waste liquor, that is to say the same in dry powder form, are introduced into and stirred with 500 parts of skim milk, in which 10 parts of β -naphthol and 10 parts of pepsin have previously been dissolved. After uniform distribution 100 parts of aniline are further introduced and the mixture is once more vigorously stirred. The mixture is heated to about 50-70° C. and combined with stirring with 10% of its total weight of a phenoplastic resol or a carbamide resin or a mixture of the two. 100 parts of colophonium are ground to powder with 50 parts of high melting mineral oil bitumen in a colloid mill and combined hot with stirring with the above sulphite waste liquor mixture.

3. 1000 parts of concentrated cellulose waste liquor are combined with stirring with 100 parts by weight of yeast or yeast-like products together with 100 parts by weight of aniline. 100 parts by weight of glutin are melted in 200 parts by weight of water and mixed with 300 parts by weight of phenol or cresol and with 100 parts by weight of birch-tar. The whole is stirred for so long with heating until a completely homogeneous mass has been produced. After cooling to room temperature 200 parts by weight of a 40% aqueous solution of formaldehyde are added. The mass is then stirred for so long whilst heating moderately once more until the smell of formaldehyde has disappeared.

4. 1000 parts by weight of concentrated cellulose waste liquor are combined with stirring with 100 parts by weight of yeast or yeast-like products as well as 100 parts by weight of aniline. 300 parts by weight of carbamide resin, 50 parts by weight of fatty alcohol consisting of 25 parts glycerine and 25 parts cetaceum, and 200 parts by weight of a 40% aqueous solution of formaldehyde are added. The whole mixture is stirred for so long with moderate heating until a uniform homogeneous mass has been produced.

5. 1000 parts of concentrated cellulose waste liquor are combined with stirring with 100 parts by weight of yeast or yeast-like products and 100 parts by weight of aniline. 150 parts by weight of phthalic acid anhydride are condensed with 150 parts by weight of glycerine and to this there are added 100 parts by weight of stearic acid and 250 parts by weight of colophonium ground in a colloid mill, which have previously been partially saponified by addition of 250 parts by weight of a caustic potash solution of 8° Bé. The whole mixture is stirred for so long with moderate heating

until a uniform homogeneous mass has been produced.

6. 150 kgs. of ground wood fibres (white ground wood and brown ground wood) are distributed in 3 cbm of water and mixed in a Hollander with 25 kg. of the binding agent produced as described in example 1 or 2. Hereupon 10 kgms. of a weakly acid precipitating liquid, consisting of 3 parts of aluminium sulphate and 3 parts of zinc chloride dissolved in 4 parts of water, are added, whereby the binding agent is precipitated upon the fibres. The paste of fibrous substances containing the binding agent is then separated upon a paper-making machine from water by means of suction and dried at a temperature of about 100°C. to laminar bodies about 2.5 cms. thick. These laminar bodies are then pressed upon heated hydraulic plate presses at a temperature of 140-150°C and a pressure of about 60-70 kgms/cm² for a few minutes into finished pressed plates of about 8 mms. thickness. The pressed plates so produced are extremely suitable for substitutes for plywood. The mechanical strengths of such pressed plates reach the following values calculated as averages:

Compressive strength----- about 2000 kgms/cm²
Bending strength----- about 500 kgms/cm²
Tensile strength----- about 350 kgms/cm²
Impactive bending

strength ----- about 8 cmkg/cm²
Ball pressure hardness after 10 secs-- about 3000
Ball pressure hardness after 60 secs-- about 2500

When employing long-fibred ground wood the values for the bending and tensile strengths increase by about 40-50%.

7. 150 kgms. of washed ground wood (that is freed from adhering cementing substance) is mixed with 3 cbm of water and 35 kgms. of the binding agent produced as described in examples 1 or 3 and the binding agent is then precipitated upon the fibre substance with 20 kgms. of a weakly acid reaction liquid consisting of 6 parts of aluminium sulphate and 6 parts of zinc chloride dissolved in 12 parts of water. The further treatment of the paste of fibrous substance containing the binding agent as far as its conversion into dried laminar bodies takes place as in example 6.

The laminar bodies of about 2.5 cms. thickness thus produced are then pressed upon hydraulic heated plate presses at a temperature of 150-160°C. and a pressure of 80-100 kgms/cm² to form pressed plates of about 6 mms. thickness. The plates thus produced may be employed for example as insulating pressed substances in the electrical art, as substitutes for various kinds of metal (bushings, toothed wheels etc.) substitutes for metal foils etc. The mechanical strengths in this case reach the following values calculated as averages:

Compressive strength-----kg/cm²-- about 2750
Bending strength-----kg/cm²-- about 800
Tensile strength-----kg/cm²-- about 500
Impactive bending strength

cmkg/cm²-- about 10
Ball pressure hardness after 10 secs-- about 3800
Ball-pressure hardness after 60 secs-- about 3300

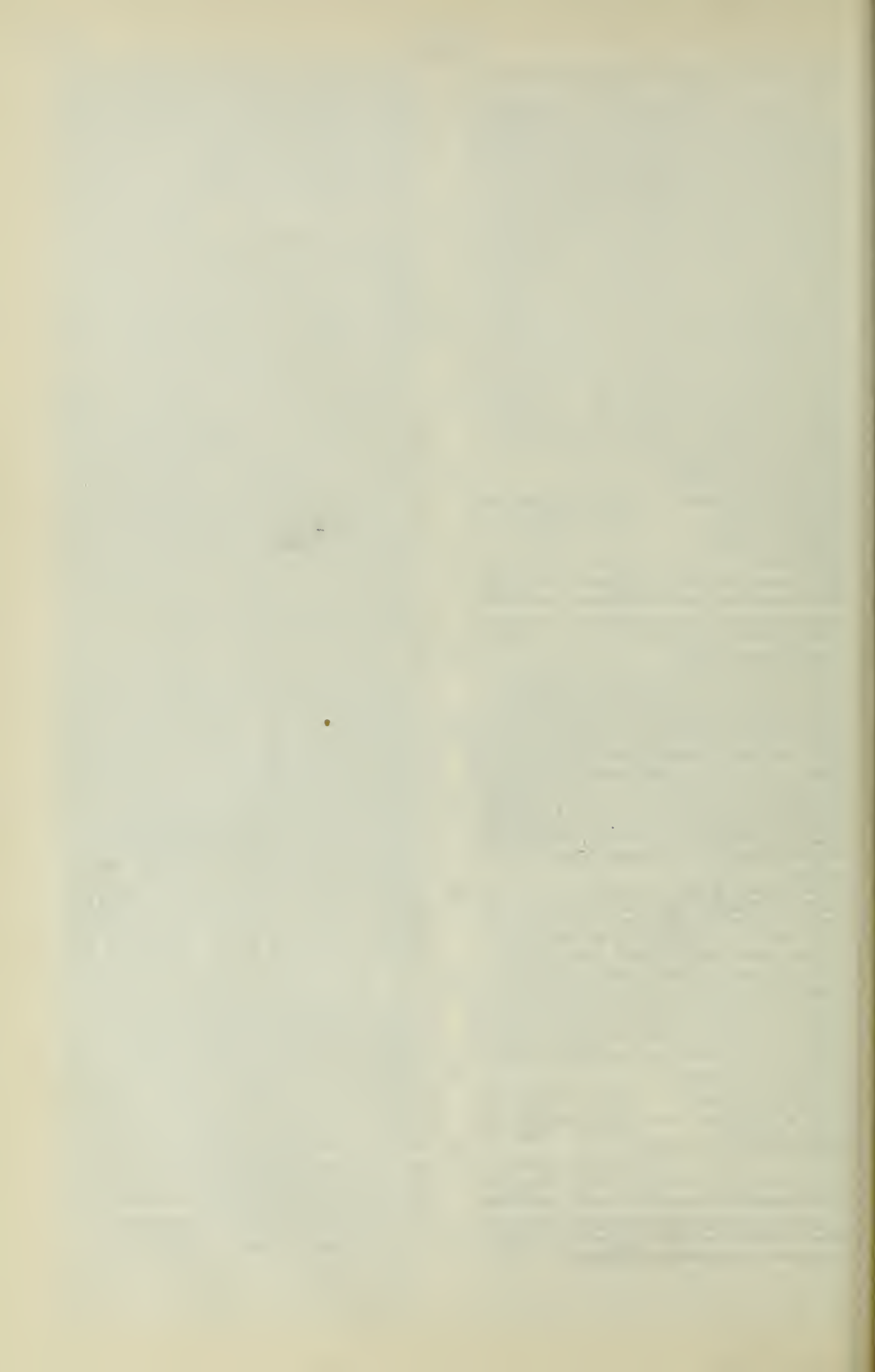
In this case also when employing long-fibred fibrous substances the tensile and bending strengths are considerably increased.

It is already known that aqueous emulsions of artificial resins or the like can be employed for steeping fibrous substances. By way of example an aqueous artificial resin emulsion produced with employment of gum arabic has been employed for this purpose. Such an emulsion does not however give up its content of artificial resin or other substances distributed in it to the fibrous substance so that on separating the liquid from the fibrous substance only those components of the artificial resin which correspond to the quantity of liquid retained by the paste of fibrous substance by absorption remain behind in the fibrous substance, in an irregular distribution and not bound to the fibrous substance. In this case therefore a very considerable proportion of the amount of additional substance dispersed in the liquid goes to waste unused.

In order to remove this disadvantage it has also already been proposed to employ emulsions or solutions of substances which may be caused to separate by addition of precipitatingly acting emulsion destroyers and thus to deposit upon the fibre the additional substance contained in the emulsion or the solution. The results obtained in this way are thoroughly useful as such and the process of depositing the substances contained in the emulsion corresponds to the method of working described above. The essential difference and the consequent technical advance of the present process depends, in contradistinction to the above, upon the use of the binding agent according to the invention. It was not known on the one hand that such binding agent emulsions could be built up upon the basis of sulphite waste liquor, and above all it was not known that such a binding agent could be so built up that not only the emulsified additional substances but above all also the emulsifier, that is to say the sulphite waste liquor or the high molecular substances contained therein, can be carried down upon precipitation and a fibrous substance loaded with binding agent thus be produced from which finished products of quite unusual mechanical and other properties can be produced. In particular also, the production of shaped bodies by heat and pressure from a fibrous substance loaded with a binding agent containing sulphite waste liquor was not known.

Finally it was also previously known that sulphite waste liquor can be condensed with phenols, amines or urea, upon the one hand and with aldehydes or ketones on the other hand, and thereby products be obtained which are water-soluble and soluble in various reagents, mostly alkalis. These products however are not binding agents of the same type as those herein described, since they are not precipitated from their solutions in a form adhering to the fibre. Such solutions on the contrary precipitate the substance which they contain in a freely suspended form not bound to the fibre and the technical effects of such products as binding agents are therefore insufficient. These known products may at the best be employed as adhesive substances, tanning agents and the like. They do not on the other hand represent a binding agent of high affinity for fibrous substances, which gives great mechanical strength to the finished products.

CARL ERNST WILLY OESTERREICH.



ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF RESITES

Emil Dreher, Ludwigshafen on Rhine, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 17, 1939

The present invention relates to new kinds of insoluble and infusible phenol-aldehyde resins of the type of resites, and a process for their manufacture.

It has already been proposed to condense phenols with aldehydes in the presence of alkaline condensation agents until the aldehyde has combined, and to mix the intermediate product thus obtained with fatty acids or acids with low electrolytic dissociation constants. Insofar as insoluble and infusible condensation products (resites) are to be produced thereby, these acids are however employed in excess.

It is known that alkali-condensed resols can only with difficulty be hardened to insoluble and infusible compact articles such as blocks, bars, tubes, plates, etc., since cracks and blisters form and the hardened product is only with difficulty removable from the mould. In addition, the cast resins show only an insufficient strength and homogeneity, so that they are not serviceable for technical purposes.

The process according to the present invention now renders it possible, in a surprising manner, to harden alkali-condensed resols, prepared from phenols and aldehydes, into cast resins characterized by extraordinarily good mechanical strength, especially high chemical resistance to organic solvents and acids, in particular inorganic acids, and to water and steam. In addition, the products are practically free from shrinkage, all of which is not the case with cast resins hitherto prepared.

In accordance with the present invention, the phenols and aldehydes, used in a molar ratio such that 1 mol. of phenol is mixed with not less than 1 mol. of aldehyde and preferably 1.25 mol. of aldehyde, are treated in known manner with alkaline condensation agents and, after easily soluble resols have been formed or the aldehyde employed has been combined, admixed with high-molecular organic fatty acids or resin acids, but only in an amount which is insufficient for complete neutralization of the alkaline condensation agents used, whereupon the hardening is effected and the final product is formed in an alkaline condition, since no acid reaction should set in during the reaction. It is preferred to neutralize about 70 to 98 per cent of the alkaline condensation agents employed. If desired, the condensation may be carried out under reduced pressure, in order to remove volatile ingredients or air from the resin. The now dehydrated condensation products are further condensed in

moulds, until the no longer varying condition of resite is attained.

Besides ordinary phenol, which is preferably employed, cresols, particularly metacresol, xylenols, particularly metaxyleneol, cresol mixtures containing metacresol and/or metaxyleneol, or mixtures containing several or all of the above mentioned phenols, resorcinol or the like, are also suitable for the process according to the present invention.

Of the aldehydes, formaldehyde or its polymers, such as paraformaldehyde, trioxymethylene, or compounds splitting off formaldehyde, are especially preferred. Other aldehydes, such as acetaldehyde, furfuraldehyde, or mixtures of various aldehydes, may also be employed.

Caustic potash solution is suitable for the alkaline condensation. Caustic soda solution, ammonia, alkali and alkaline-earth hydroxides, quaternary ammonium bases, aromatic and aliphatic amines containing at least two carbon atoms, etc., may however also be employed in the condensation. All alkaline condensation agents are suitable, which, with the organic fatty acids or resin acids employed, are ultimately capable of forming salts which are gel-soluble in the resins and have an emulsifying action.

Of the organic high-molecular fatty acids or resin acids which may be employed, there may for example be mentioned oleic acid, palmitic acid, stearic acid, ricinoleic acid, linseed oil fatty acid, train oil fatty acid, abietic acid, copal resin acid, tall oil acid, coconut oil fatty acid, palm kernel oil fatty acid, wool grease fatty acid. It is preferable to use those fatty acids which contain more than 12 carbon atoms in the molecule and which are capable of forming, with the bases used for condensation, salts which are gel-soluble in the resins and have an emulsifying action.

For the condensation and hardening, the usual temperatures are employed, these being about 40 to 100°C. for the condensation and 40 to 170°C. for the hardening. The duration of heating varies according to the amount of condensation agent employed, and depends on the molar ratio of phenol to aldehyde employed and also on the operating temperature.

The cast resin resites prepared by the process according to the present invention are characterized by an extraordinarily high power of resistance to chemical action, and are stable to moisture, water and steam, and also to organic solvents, acids, even concentrated mineral acids, fatty acids and the like. Products prepared according to the invention were treated with con-

centrated sulphuric acid, concentrated hydrochloric acid, concentrated phosphoric acid, concentrated formic acid, or with aqua regia, for 50 hours at 90°C without their being attacked or altered. Hitherto known phenol-aldehyde resins, after such treatment, were either completely destroyed or were extremely strongly attacked.

The products obtained according to the present invention do not become cracked, and exhibit an extraordinarily high strength. Thus the impact bending strength amounts to 26 to 28 cmkg/cm². This strength was measured on a standard bar and is 2 to 4 times as great as that of condensation products hardened in an alkaline state to the end without addition of fatty acids. (Details of the method of determining strengths is to be found in *Vorschriftenbuch des Vereins Deutscher Elektrotechniker*, 1933, p. 401.) The bending strength of the new products shows a value of about 1420 cmkg/cm², whilst hitherto known products show a value of only 450 to 900 cmkg/cm². The heat resistance, measured according to Martens (for details of this method see *Vorschriftenbuch des Vereins Deutscher Elektrotechniker*, 1933, p. 404), amounts to 120 to 130°C., as compared with a heat resistance of 45 to 100°C. for known products. The notch impact strength, which gives a measure of the brittleness of artificial materials (details are to be found in the article by Nitsche and Zebrowski in the periodical "*Plastische Massen*," 1937), is 1.7 to 1.9 kgcm², whilst artificial resins condensed in an alkaline state to the end without addition of fatty acids show only values below 1. The ball test hardness is 1350 kg/cm², as against 600 to 1000 kg/cm² for known materials.

The stability of volume of the new resins is noteworthy, i. e., they are practically free from shrinkage. In addition, they may be worked mechanically in the usual manner and quite as easily as are the hitherto known artificial resins of the cast resin type.

Owing to the above mentioned properties the products manufactured according to the present invention are suitable for a great variety of technical applications, particularly as substitutes for metals, for the manufacture of bearings, and for all purposes for which a material resistant to chemical action is required, for example, for the construction of acid pumps, acid containers, chemical apparatus, and the like.

The process according to the present invention will be further illustrated by the following examples, but it is to be understood that the invention is not to be restricted to the initial materials and working conditions employed in these examples.

Example 1

1000 grams of phenol and 1250 grams of 33 per cent formaldehyde are condensed with 100 cc of 5N-caustic potash solution, until the whole of the formaldehyde has combined. When using a temperature of 80°C., this will be the case after about 1 to 2 hours. A slightly reduced pressure of about 500 mm of mercury is maintained in the reaction vessel. The water is then removed by distillation in vacuo, and the intermediate product obtained is admixed with 138 grams of oleic acid. The product, after being concentrated to a viscous condition, is then hardened in moulds in the manner customary in the manufacture of cast resins, at a temperature of about 100°C.

Example 2

1000 grams of phenol and 1000 grams of 33 per cent formaldehyde are condensed with 100 cc of 5N-caustic potash solution, as described in Example 1. After removal of the water, 135 grams of ricinoleic acid are added, whereupon the mixture is further treated as in Example 1.

EMIL DREHER.

ALIEN PROPERTY CUSTODIAN

SOLVENT FOR POLYMERISED SYNTHETIC SUBSTANCES

Paul Kümmel, Oranienburg, near Berlin, Germany; vested in the Alien Property Custodian

No Drawing. Application filed June 14, 1939

The present invention relates to solvents for polymerised synthetic substances and particularly to synthetic substances of this kind containing chlorine such as chlorine-rubber and polymerised vinyl chloride. These substances, as is known, are continuously increasing in importance but it is difficult to obtain pore-free films with such substances so that their high resistance cannot generally be sufficiently utilised.

The present invention renders it possible to obtain pore-free coatings with such substances when they are used in certain solvents which have the further advantage that they can also dissolve polymerised compounds free from chlorine such as polystyrenes and alkyl cellulose or other cellulose ethers.

Contrary to the usual aromatic and nitrogen-containing synthetic substances, the said aliphatic and arylaliphatic synthetic substances, but principally synthetic substances of this kind containing chlorine, have a very low solubility in the usual solvents, and a particularly low solubility with the fairly volatile solvents preferably used in the lacquer or varnish industry. Whereas for example other synthetic substances can be easily or fairly readily dissolved in commercial benzene, with these synthetic substances this can be done only to an extent which is quite insufficient for practical purposes.

It has now been found that of the aromatic solvents, methylisopropylbenzene occupies a special position since this aromatic substance which is characterised by its relatively large aliphatic substituted part can dissolve such synthetic substances in considerably greater quantities. Accordingly the present invention consists in a medium to difficultly volatile solvent for polymerised synthetic substances of the aliphatic or arylaliphatic series, particularly for halogen-containing synthetic substances of this kind such as chlorine-rubber or polymerised polyvinylchloride consisting in a solvent mixture comprising methylisopropylbenzene. Although in practice the speed of solubility is sufficient only for polystyrenes, methylisopropylbenzene becomes generally utilisable when small quantities of aliphatic ester or ketones are added thereto. This addition can be maintained below 10% so that upon drying such solvent mixtures no undesired disintegration phenomena arise since the speeds of evaporation of the components are in this case approximately equal. As esters and ketones the following for example have been shown to be utilisable as solvents, a certain superiority of the oxycarbonic acid esters over the remaining sol-

vents being clearly recognisable: ethyl acetate, butyl lactate, butyl acetate, ethyl oxalate, ethyl glycol acetate, butyl propionate, methyl ethyl ketone, diamyl ketone, mixtures of glycolmonoacetate with a higher alcohol such as butanol or ethyl glycol. Even for the difficultly soluble chlorine-rubber an addition of 7.5% ethyl lactate is in this case sufficient.

As is known, esters and ketones are good solvents for most synthetic substances and thus also for certain synthetic substances of the kind dealt with here. It must nevertheless be considered as surprising that, contrary to what is otherwise known, the addition of methylisopropylbenzene does not give rise to any precipitation of the dissolved substance from such solutions. It would normally be expected that this aromatic substance, like the usual aromatic substances, would abstract the aliphatic solvent from the solution of synthetic substance and thus cause precipitation of the said synthetic substance. That in the present case this unexpected effect occurs appears to be due to the fact that this aromatic compound comprises extensive side chains which themselves condition the stability of the system. This must be correct as is shown by the fact that isopropylbenzene seems to have a similar favourable effect. It appears to be due to the same reason that during the drying of the varnish, and thus the evaporation of the solvent, disintegration cannot normally be observed.

In this way there is obtained a solvent for the said polymerised substances which is of only medium volatility and therefore of good use in the varnish industry, and which above all is also cheap since, as is known, methylisopropylbenzene is formed as a waste product in the production of cellulose from wood and in the extraction of camphor. It is especially to be emphasised that this solvent is especially suitable for polymerised substances containing halogen, particularly chlorine-rubber. The varnish formed from a base of for example chlorine-rubber (for example that known under the registered Trade Mark "Tegofan") is not at all or only very slightly inclined to become stringy when spread or sprayed and provides pore-free coatings or films. Even with the addition of the known solvents for varnishes, viz. commercial benzene or ester-benzene mixtures this undesired phenomenon does not appear. Such varnishes flow well and the gloss obtained is even outstanding. Almost the same effect is obtained with polymerised vinyl chloride, (for example that known under the registered

Trade Mark "Vlnoflex N") or polymerised styrene, (for example that known under the registered Trade Mark "Ronilla L"). In the series of hitherto utilisable fairly or difficultly volatile solvents such cheap and generally utilisable solvents did certainly not exist.

The invention is illustrated by the following examples, but it is to be understood that the invention is not restricted to the particular details disclosed therein.

Example 1.—92 parts by weight methylisopropylbenzene are mixed with 8 parts by weight ethyl lactate. This mixture is especially suitable for chlorine-rubber.

Example 2.—93 parts by weight p-methylisopropylbenzene are mixed with 7 parts by weight ethyl benzol propionate. This solvent is well suited for polymerised vinyl chloride and also for other polymerised resins.

Example 3.—90 parts by weight methylisopropylbenzene are mixed with 10 parts by weight

diamyl ketone. Since methylisopropylbenzene is formed in cellulose manufacture and processes, such mixtures are quite cheap, so that the cost of an addition of such a somewhat dearer ketone can be borne.

Example 4.—35 parts by weight p-methylisopropylbenzene are mixed with 10 parts by weight isopropylbenzene (or instead 10 more parts p-methylisopropylbenzene) 5 parts by weight butyl lactate, 25 parts by weight benzene lac and 25 parts by weight butyl acetate. This mixture appears to be especially economical, and is suitable for all purposes within the scope of the invention.

Example 5.—46 parts by weight methylisopropylbenzene are mixed with 4 parts by weight ethyl oxalate and 50 parts by weight toluene. This makes a cheap solvent which is almost generally utilisable for the objects mentioned.

PAUL KÜMMEL.

ALIEN PROPERTY CUSTODIAN

GLUCOSIDIC COMPOUNDS

August Chwala, Vienna, VII, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed July 7, 1939

This invention relates to novel compounds of a glucosidic nature and to a process for the production of compounds of a glucosidic nature.

An object of my invention is to obtain compounds of a glucosidic nature, which are inter alia particularly useful as cleansing, washing and wetting agents in the textile industry and similar fields of manufacture, and further as dispersing, emulsifying and protecting agents and the like.

Another object of my invention is to provide a method for producing compounds of a glucosidic nature which is practicable in a commercial scale.

Other objects will appear from the following detailed description.

For the production of compounds of a glucosidic nature of higher molecular weight the procedure hitherto adopted in practice has been either to heat acetylated monosaccharides with higher molecular alcohols in the presence of condensing agents such as zinc chloride, or to react upon aceto sugar halides with higher alcohols in the presence of acid binding agents. In both cases the sugar hydroxyls blocked by acetylation are subsequently set free by hydrolysis.

The etherification of sugars with higher molecular alcohols, of which the fatty alcohols come primarily into consideration for the purpose of obtaining capillary active compounds, gives rise to very considerable technical difficulties owing to the reluctance of sugars to react with alcohols of fatty character.

The present invention is based on the principle of etherifying sugars with alcohols having a relatively short carbon chain, which contain a reactive halogen atom, and thereby of the halo-alkyl glucosides thus formed to combine with further organic group to form higher molecular compounds. The method according to the invention thus consists broadly in converting alcohols of low molecular weight containing reactive halogen, to alkyl glucosides, and, if the object is to obtain high molecular, particularly capillary active substances, in coupling the alkyl glucosides directly or indirectly with organic, preferably high molecular organic compounds, in the same or a separate working operation, with the aid of the reactive group. The method according to the invention leads to a large number of new compounds of a glucosidic nature which are all characterised by the feature that they have a low alcohol in glucosidic link, which, in its turn, is capable of being esterified, etherified, or, with the interaction of an amino group, of being acetylated or alkylized. The alkyl-glucosides pre-

pared in accordance with the invention, which contain reactive halogen in the alcohol radical afford, first and foremost, the possibility of obtaining, by selection from the multifarious further organic compounds to be coupled with the aid of these groups, high molecular, novel compounds, the properties of which can be adapted to suit particular uses by appropriate selection of the components used in the coupling stage, or by subsequent modifying the compounds obtained by the coupling of the components particularly with substitution of reactive hydrogen atoms present in said compounds by substituents influencing the solubility in water.

Without it being necessary to effect temporary blocking of the sugar hydroxydes, the glucosides formation proceeds very easily and smoothly, and this constitutes a very significant advantage of the invention from the point of view of its practical realisation on a technical scale.

The following substances are suitable for example as the sugar constituent of the alkyl-glucosides according to the invention: Pentoses (e. g. arabinose and xylose); hexoses (e. g. glucose, fructose, galactose); furthermore, disaccharoses (e. g. milk sugar, cane sugar); polysaccharoses (e. g. starch, dextrin.) intramolecular anhydrides of sugars and further technical products rich in sugar such as starch sugar or wood sugar.

Low molecular alcohols useful for effecting the glucosidification, and containing at least one reactive halogen atom, are for example: glycol-chlorohydrin $\text{CH}_2\text{Cl}-\text{CH}_2\text{OH}$, glycol-bromohydrin $\text{CH}_2\text{Br}-\text{CH}_2\text{OH}$, propylene-chlorohydrin $\text{CH}_3\text{CHOH}-\text{CH}_2\text{Cl}$, glycerol-chlorohydrin



glycerol-bromohydrin $\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{Br}$, glycerol-alfa, gamma-dichlorohydrin, glycerol-alfa, gamma-dibromohydrin, monochloroether of di- and polyglycol and polyglycerol.

The glucosidification is effected by causing the sugar component to react with the halogen containing low molecular alcohols and more particularly with the halohydrins, the alcohols being present in excess and the said reaction being carried out while applying heat and in the presence of an acid catalyst. The following substances are particularly suitable for use as catalysts: sulphuric acid, sulphuric acid in commixture with primary sulphate, phosphoric acid, and phosphoric acid in commixture with primary phosphate, perchloric acid, sulfonic acids, such as benzene-sulfonic acid, sulfotoluenic acid,

naphthalenesulfonic acid, di-iso-butyl-naphthalenesulfonic acid, isethionic acid, further more, carboxylic acids, e. g. oxalic acid, trichloroacetic acid and the like, which all have less tendency to exert a reversing action than hydrochloric acid. After completion of glucosidification the acid is partially neutralised with sodium carbonate, sodium bicarbonate, secondary sodium phosphate or the like, after which the surplus halogenohydrin is distilled off, preferably in a vacuum. The hydrochloric acid which keeps also being split off in small quantities from the halogenated alcohols, and which has a marked tendency to diminish the yield of the reaction, is neutralised by the further addition of sodium carbonate or bicarbonate, secondary sodium phosphate or the like, prior to the distilling off of the halogenohydrin. The crude glucosides obtained are syrupy to vitreous masses which are generally obtained with a glucoside content of 70 to 80%, and which are suitable in this form for being subjected directly to further reactions.

Examples of reactable compounds capable of being combined with these halogeno-alkyl glucosides are higher molecular carboxylic acids, phenols, proteins, sulphonic acids, and amines.

As carboxylic acid there may be used higher fatty acids, resinic acids and naphthenic acids, the salts of which react to form higher molecular ester glucosides, e. g. with beta-chloroethyl glucosides, in accordance with the Equation



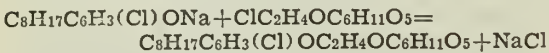
R denoting a higher hydrocarbon group or radical.

As fatty acids, not only the acids obtainable from vegetable and animal fats are suitable but also their saturated derivatives obtained by hydrogenation and also the carboxylic acids obtainable by oxidation of higher hydrocarbons such as crude petroleum, distillation tar, or paraffin.

Further, the above-mentioned halogen containing glucosides are also capable of being combined with the alkali salts of higher molecular phenols, preferably with those the hydroxyl group of which is more pronouncedly acid than is the case with nucleohalogenated derivatives or with the phenols having a plurality of hydroxyl groups.

The higher molecular phenols are obtainable, by a mode of reaction known per se, for instance from phenol or cresol and olefines, by condensation. Benzene obtained by cracking affords a suitable source of these olefines.

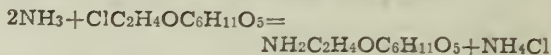
By combining of the above-mentioned phenolates with beta-chloroethyl glucoside there are obtained ether glucosides, for instance in accordance with the Equation



The aromatic nucleus contained in this compound therein may, if desired, be converted by hydrogenation into a saturated ring. As an example of an easily obtainable higher molecular phenolic body there may be used lignin which reacts readily with halogenated glucoside in alkaline solution.

Albuminous bodies, preferably such as of an acid character, are capable, in the form of their metal compounds, of being coupled with halogen-alkyl glucosides. Examples of such albuminous bodies are casein, protalbinic acid and lysalbinic acid.

A further possibility of coupling hydrocarbon radical with sugars consists in converting halogenated glucosides, by heating with ammonia or amines under pressure, into amino-glucosides and acylating these latter in the amino group by reacting thereupon with higher carboxylic acids. Thus, in accordance with the Equation:



from beta-chloroethyl glucoside and ammonia there becomes formed beta-aminoethyl glucoside, into the amino group of which there may be introduced an acyl radical by treatment with higher fatty, resinic or naphthenic acids or with halides or anhydrides thereof, if desired or necessary in the presence of acid neutralising agents such as soda, potassium lye or the like. Instead of halides of higher carboxylic acids there may also be employed the halides of aromatic sulphonic acids preferably having one or more side chains of considerable length in the aromatic nucleus.

Finally, higher hydrocarbon radicals may be combined with sugars by way of the described halogenated alkyl glucosides, for example of beta-chloro- or bromo ethyl glucoside, by a converting the said beta-chloro- or bromoethyl glucoside with higher molecular amines, e. g. with dodecylamine, aminoparaffin (obtained from chloroparaffin by conversion with ammonia) or with nitrolamines obtained from terpene hydrocarbons.

If beta-aminoethyl glucoside or beta-methylamino glucoside or similar compounds be used higher molecular glucosides are obtainable by reacting with higher molecular alkyl halides, e. g. octadecyl bromide, chloro-paraffin, higher molecular chlorohydrins such as may be obtained from olefines resulting from the cracking of hydrocarbons, by the adding on of hypohalogenic acid, and the like; these higher molecular glucosides may also, if desired, be quarternized.

Finally, amino-alkyl glucosides may be condensed with phenols in the presence of formaldehyde, whereby N-oxybenzylated amino ethyl glucosides are obtained.

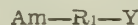
The products obtainable by the methods specified may be classified as belonging to the following three classes of glucosidic compounds:

1. Halogeno-alkyl-glucosides corresponding to the formula



wherein Hal is a halogen such as chlorine or bromine, R_1 is a bivalent low molecular alkyl radical having 2 to 5 C atoms directly bound to each other and Y is a sugar group glucosidically combined with the alkyl radical R_1 .

2. Amino-alkyl-glucosides corresponding to the formula

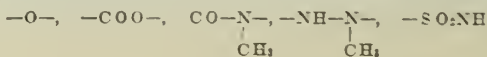


wherein Am is an aminic radical, e. g. NH_2- , $\text{NH}(\text{OH})-$, $\text{NH}(\text{C}_2\text{H}_4\text{OH})-$, $\text{N}(\text{CH}_3)_2-$, R_1 is a bivalent low molecular alkyl radical having 2 to 5 C atoms directly bound to each other and Y is a sugar group glucosidically combined with the alkyl radical R_1 .

3. High molecular glucosides corresponding to the formula



wherein R is a high molecular hydrocarbon radical containing at least 6 C atoms, X is a linking group, e. g.



or the like, R_1 is a low molecular alkyl radical having 2 to 5 C atoms directly bound to each other, and Y is a sugar group glucosidically combined with the alkyl radical R_1 .

The low molecular alkyl radicals R_1 as well as the high molecular hydrocarbon radicals R referred to in the above specified formulae may contain various substituents.

The high molecular glucosides corresponding to the formula $R-X-R_1-Y$ may be modified and more particularly modified in respect to their surface activity by replacing reactive hydrogen atoms present either in the sugar group (Y) or in the alkyl radical (R_1) or in the linking group (X) or in two or all of these groups by hydrophilic or hydrophobic groups. The substitution of such reactive hydrogen atoms by hydrophilic or hydrophobic groups may be carried out either before the synthesis of the said high molecular compounds of a glucosidic nature by introducing either hydrophilic or hydrophobic groups into the components to be combined or by reacting upon the glucosides yet synthesized. Especially the solubility of the high molecular glucosides produced in accordance with this invention may be influenced in a controllable manner by such modifying operations.

The substitution of reactive hydrogen atoms by the introduction of groups influencing the surface activity of the high molecular glucosides may be effected in the case an increase of the hydrophilic properties being aimed at for instance by the following methods of treating the high molecular glucosides or its components.

a. By a treatment with 1, 2 alkylene oxides e. g. ethyleneoxide, propyleneoxide and the like or epichlorohydrine.

b. By a treatment with chlorohydrins e. g. ethylenechlorohydrin, glycerinechlorohydrin, polyglycol- or polyglycerolchlorohydrin.

The treatment with chlorohydrins may be effected in the case of a reactive hydrogen atom being present in the linking group X and being bound to a basic nitrogen atom. In this case the reactive hydrogen atom may also be replaced by a hydrophilic group by treating the glucosidic compound with an alkyl glucoside corresponding to the formula referred to above sub 1. In this way of proceeding products are obtained containing two hydrophilic sugar groups combined with one hydrophobic high molecular hydrocarbon radical.

c. An increase of the hydrophilic properties of the glucosidic compounds may furthermore effected in the case the linking group X containing a basic nitrogen atom by quaternation.

d. By introducing radicals of inorganic acids e. g. sulfuric acid, phosphoric acid, pyrophosphoric acid and other radicals of equivalent acids.

e. By introducing a carboxylic group by oxidation of a primary sugar hydroxyl group to a carboxyl group. An enhancement of the hydrophilic properties is achieved in this case if the linking group X is free from a basic nitrogen atom.

The substitution of reactive hydrogen atoms by hydrophobic groups for the purpose of enhancing the hydrophobic properties may for instance be carried out according to the following methods:

f. By complete or partial alkylation, for instance by means of dimethylsulfate, benzylchloride, etc. in the case of the linking group X being free from a basic nitrogen atom.

g. By the action of carbonyl compounds or agents easily splitting of carbonyl compounds e.

g. aldehydes such as formaldehyde, acetaldehyde, paraldehyde, acroleine, chloroacetaldehyde, chloral, acroleinedibromide or ketones such as acetone, chloroacetone and the like.

h. By complete or partial esterification with low molecular acid chlorides e. g. benzylchloride, acetylchloride, or low molecular acid anhydrides e. g. acetic acid anhydride.

i. By replacement of reactive hydrogen atoms contained in the linking group X by low molecular hydrophobic radicals e. g. by a benzyl radical. In the case of the linking group X containing a basic nitrogen atom the hydrophobic properties are enhanced if the hydrophobic radicals contain an anionactive group, for example if the reactive hydrogen atom is caused to interact with monochloroacetic acid, chlorooxypropene sulfonic acid.

The higher molecular glucosides obtained by the described reactions are soluble in water of neutral reaction; the solutions are frothy and are unsensitive to hardening principals in water, alkaline solutions, and dilute acids in the concentrations used in the textile industry, as also the solutions of metal salts. They possess good qualities as dispersing agents for dye pigments and the like and are colloid protecting agents e. g. for protecting freshly formed calcium soap against flocculation and may be used as washing, wetting, and cleansing agents, even in acid baths or baths containing metal salts. The addition of substances of this kind to mercerising liquors has a favourable effect on the wetting and shrinking of cellulose fibres. In concentrated aqueous solutions they have valuable emulsifying properties in respect to vegetable, animal and mineral oils and also fatty acids; mixtures of fatty acids and oils can also with advantage be finely dispersed with their aid.

If the compounds according to the invention be added to dye baths a retarding of the dyeing action is obtained, particularly in vat dyeing. By "soaping" vat and naphthol dyes with higher molecular glucosides bright clean colours are obtained which are fast to rubbing. The compounds of a glucosidic nature containing high molecular fat-chains impart to textile materials treated therewith a pleasing, soft and springy texture.

Those of the above-described compounds which have a plurality of free phenolic hydroxyl groups are useful as tanning auxiliary agents.

Examples

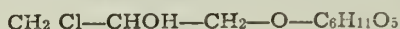
1. 80 parts of anhydrous glucose are heated with 380 parts of anhydrous glycolchlorohydrin and 7 parts of a mixture of 50 parts of phosphoric acid, 89 per cent strong, and 6 parts of caustic soda, to a temperature of 100°C with agitation and frequent shaking, until a sample only slightly reduces Fehling's solution. If the phosphoric mixture be replaced by 2 parts of concentrated sulphuric acid this state is reached after about three hours. To the resulting yellow solution, when cold there is added a concentrated aqueous solution of 7 parts of calcined soda, after which the excess chlorohydrin is distilled off as rapidly and completely as possible in a vacuum; finally, this mass is heated in vacuum for about 45 minutes, to a temperature of 110 to 120°C. The residue, which gives an alkaline reaction with litmus, is dissolved in hot alcohol, filtered to remove undissolved salts, after which the alcohol is evaporated until a yellowish solid mass, capable to pulverize is obtained, the yield being 117 parts with

64 per cent of beta-chloroethyl glucoside. To prevent yield-reducing reversal of the reaction small quantities of a soda solution are added if necessary at frequent intervals during the working up of the glucoside, and, also if necessary, a small quantity of secondary sodium phosphate, to neutralise any acid reaction that may arise. Instead of 380 parts of glycol-chlorohydrin there may be used with otherwise unchanged proportions 590 parts of anhydrous glycol-bromohydrin.

In place of the mixture referred to above consisting of phosphoric acid and primary phosphate or in place of sulfuric acid a mixture of 2 parts of sulfuric acid and 1 part of sodiumbisulfate or 5 parts of perchloric acid or 4 parts of benzenesulfonic acid or naphthalenesulfonic acid or diso-butyl-naphthalene sulfonic acid may be used.

2. 80 parts of glucose are treated with 400 parts of glycerolmonochlorohydrin and 2 parts of concentrated sulphuric acid, as in Example 1. After the addition of the soda solution the surplus glycerol monochlorohydrin is distilled off in a vacuum to such an extent that the residue constitutes a thin syrup which is stirred up repeatedly with anhydrous acetone for the purpose of removing any glycerol monochlorohydrin that may still be present therein.

After drying off any still adhering acetone by heating in a vacuum there is obtained a vitreous mass, the main constituent of which is gamma-chloro-beta-oxypropyl glucoside



The mass obtained contains some 68 per cent of this glucoside.

3. 30 parts of lactic sugar are heated with 100 parts of glycolchlorohydrin and one part of concentrated sulphuric acid for 3½ to 4 hours, with frequent stirring to a temperature of 90 to 95°C. After this time the reaction with Fehling's solution has disappeared. There is then added to the mixture a solution of 1.2 parts of soda in 3 parts of water, and the surplus chlorohydrin is distilled off in a vacuum. The further working up is effected in accordance with Example 1. There is obtained a yellow solid mass containing 71 per cent of a mixture of beta-chloroethyl glucoside and beta-chloroethyl galactoside.

4. 100 parts of anhydrous wood sugar rich in pentoses are heated with 400 parts ethylenchlorohydrin and 4 parts concentrated sulfuric acid or 8 to 10 parts oxalic acid or trichloroacetic acid, while stirring, over a waterbath until a Fehling's solution is not more or only slightly reduced by the reaction mixture. Further working is carried out as described in Example 1. A reaction mixture is obtained containing some 80% halogeno-alkyl-glucoside.

5. Beta-chloroethyl glucoside is produced by heating to 95°C for 10 to 12 hours and stirring a mixture of 20 parts of dried starch, 100 parts of ethylene chlorohydrin and 1 part of concentrated benzenesulphuric acid; the further working up is effected as in Example 1.

6. 121 parts of a 54 per cent beta-chloroethyl glucoside are heated with 240 parts of concentrated aqueous ammonia for 2 hours under pressure to a temperature of 115–120°C. After the addition of 1.5 parts caustic soda the mixture is evaporated to half its volume, filtered, and concentrated in a vacuum, the temperature of the residue being retained for ½ to ¾ hour at a temperature of 105°C. The residue is then dissolved in water, and yields 170 parts of a clear brownish

liquid containing some 54 parts of beta-aminoethyl glucoside.

7. 51.4 parts of 74 per cent beta-chloroethyl glucoside are converted with 180 parts of 13 per cent methylamine for 2½ hours at a temperature of 110°C and further worked up in accordance with Example 6. After the addition of 7 parts of sodium hydroxide there are ultimately obtained 90 parts of a solution containing some 33 parts of beta-methylaminoethyl glucoside.

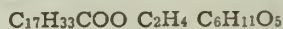
8. 3.7 parts of the glucosidic mixture according to Example 3 are dissolved in 4 parts of water, after which 2 parts of diamylamin and 7.5 parts of alcohol are added, and the mixture heated under pressure and with agitation, for 4 to 5 hours to a temperature of 130°C. After cooling, 4.4 parts of caustic soda dissolved in 10 parts of water are added, and the alcohol and surplus amine are distilled off, the resulting clear solution containing diamylaminoethyl glucoside.

9. 2.5 parts of beta-chloroethyl glucoside, 64 per cent strong, according to Example 1

0.04 part of calcined soda, pulverized

1.5 parts of anhydrous pulverised oleic soap

are intimately mixed together in an open vessel and heated to a temperature of 140°C. The mixture is maintained at this temperature until a sample dissolved in water has at the most a weakly opalescent effect after acidification, which will be the case after heating for about ½ hour. There is obtained a yellowish mass which sets when cold, and which consists in the main of the ester glucoside:



This compound dissolves in water, yielding a clear frothing liquid. Instead of oleic soap an equivalent quantity of naphthenic soap may also be used, and in this case the corresponding ester glucoside is obtained.

10. 3.3 parts of chloroxypropyl glucoside, 68 per cent strong, according to Example 2, are stirred with 2.5 parts of water, with the application of heat, until thickly liquid, and mixed with a mixture of 1.5 parts of chloroethyl phenol, 0.55 parts caustic potash, 0.6 parts of water and 2.5 parts of alcohol, and heated for three hours in a water bath. After conversion, there is obtained the chloroktyl phenol ether of ethylol glucoside, which is soluble in water. Chloroktyl phenol is obtained by condensing phenol with an olefinic cracked benzene (boiling point 125–145°C) in a manner known per se, fractionating and chlorinating the condensation product consisting in the main of octyl phenol.

11. 8 parts of alkali lignin purified by precipitation are dissolved in 30 parts of water with the aid of 1 part of NaOH; 8.5 parts of beta-chloroethyl glucoside, 70 per cent strong, are added, and the clear mixture boiled for about ten hours on a reflux condenser after which a sample when diluted with water and treated with a few drops of acetic acid remains clear.

12. 3.8 parts of isobutyl lignin (according to Haegglung, "Cellulosechemie 1927, page 72) are dissolved in 9.2 parts of a 6.5 per cent caustic soda solution, and after the addition of 4 parts of 76 per cent beta-chloroethyl glucoside, boiled on a reflux condenser until a sample in water gives no precipitate after acidification with acetic acid, which is the case after some 1 to 1½ hours.

13. 55 parts of caseine are dissolved with 2 parts of sodium hydroxide in 140 parts of water. 22.5

parts of the caseine solution are mixed with 7 parts of 72 per cent beta-chloroethyl glucoside and heated for 1½ hours to a temperature of about 95°C. There is obtained a mass which is thick when cold and which dissolves in water to form an opalescent solution.

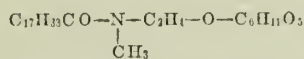
14. 7.8 parts of beta-methylaminoethyl glucoside solution, 33 per cent strong, according to Example 7 are admixed with a solution of 0.5 parts of calcined soda in two parts of water, immediately followed by the addition of 3 parts of octyl benzene sulfochloride. The mixture is thoroughly agitated and gradually heated to a temperature of 50 to 60° C, at which temperature it is retained for about ½ hour while stirring. The mixture, which is initially cloudy, becomes clear and thick. It then dissolves in water yielding a clear to weakly opalescent solution, the effective constituent of which being octylbenzenesulfomethylaminoethyl glucoside. The octyl benzene is obtained by condensing the olefines of a cracked benzene (boiling point 125–145°C) with benzene in a manner known per se, using aluminium chloride as catalyst. The fraction passing over at 235–245°C, which consists mainly of octyl benzene, is then converted into sulfochloride by means of chloro sulphonic acid.

15. 6.5 parts of beta-aminochloroethyl glucoside solution, 33 per cent strong, 1 part of formaldehyde solution, 35 per cent strong, and 1 part of phenol are mixed together and heated for 8 to 10 hours to a temperature of 75 to 80° C. The small quantity of unaltered phenol is driven off with steam leaving a residue of solution of oxybenzylaminoethyl glucoside.

16. 13 parts of the solution according to Example 6 are mixed with 16 parts of water and 30 parts of alcohol, after which at a temperature below 15° C there is introduced, drop by drop, while stirring, a solution of 4.3 parts of lauric acid chloride, alternating with a solution of 1.4 parts of calcined soda and 8 parts of water. After evaporation of the solvent and dissolving of the residue in water there is obtained a clear frothing solution of laurylaminoethyl glucoside which remains unaffected by the addition of dilute alkaline solutions and dilute acids. Only boiling for several hours with dilute sulphuric acid (5 grams per litre) effects partial hydrolysis.

17. 13.5 parts of the solution according to Example 6 are admixed with 20 parts each of alcohol and water, and a solution of benzene is introduced, drop by drop, with agitation, at a temperature of 10 to 15° C. To neutralise the hydrochloric acid evaporated, a solution of 1.5 parts of calcined soda in 8 parts of water is, at the same time, introduced.

After evaporation of the alcohol and benzene there is obtained a residue consisting substantially of oylmethylaminoethyl glucoside of the formula



This residue gives a clear solution in water and is unaffected by dilute alkaline solutions and acid.

18. 8.5 parts of a beta-aminoethyl glucoside solution according to Example 6 are mixed with 2.5 parts of stearic acid, heated in a vacuum first of all for driving off the solvent, and then for a longer time to a temperature of about 160–170° C, until a sample dissolved in water does not become clouded or only becomes clouded to a slight extent. On the addition of acid the substance obtained is

a brownish mass consisting in the main of stearylaminioethyl glucoside.

19. 15 parts of beta-aminoethyl glucoside solution obtained in accordance with Example 6 are mixed with 10 parts of alcohol, after which a solution of 2.5 parts of abietinic acid chloride in 10 parts of benzene is added, drop by drop, while agitating and cooling the solution to a temperature of 5 to 10° C. After driving off the solvent there is obtained a clear yellow solution containing abietinyl aminoethyl glucoside. The glucoside, owing to the size of its hydrocarbon residue which is linked to the sugar, is difficultly soluble in water but is readily retained in solution by resin soap still present. On the other hand, it tends to prevent the precipitation of resin soap by constituents causing the hardness of water.

20. 1 part of sodium hydroxide is added to 50 parts of a solution of a rape seed oil fatty acids-methylaminoethyl-glucoside and -galactoside, obtained from chlorides of rape seed oil fatty acids and a mixture of methylaminoethyl-glucoside and methylaminoethyl-galactoside, the said solution being 20 per cent strong. Ethylene oxide is introduced into this solution until the increase of weight amounts to 3 parts. The wetting power of the glucoside treated in the manner described above is far better than that of the untreated product.

21. 100 parts of a solution of stearylaminioethyl-arabinoide (5 per cent strong) are allowed to react with 0.25 parts of sodium hydroxide and 4 to 5 parts of propylene oxide. The solution of the reaction products thus obtained has an increased washing capacity when compared with the untreated product.

22. 3 parts of sodium acetate are added to 50 parts of a mixture of a stearyl- and a palmitoyl-methylaminoethyl-glucoside (obtained by reacting upon a methylaminoethyl-glucoside with acid chlorides of commercial stearine), the said solution being 10 per cent strong. Bromine water, saturated in the cold is gradually introduced into this solution in such an amount, that about 2 parts of bromine are used in total. The oxydation of the primary sugar hydroxyl group proceeds only slowly, so that the reaction mixture has to rest for 1 to 2 days at about 30° C. The solution produced by this method has an improved purifying effect in washing soiled cotton than the untreated product.

23. 14 parts of sodium hydroxide are added to 100 parts of a dispersion of stearylaminioethyl-glucoside, 20 per cent strong, and shaken with 40 parts of dimethyl sulfate introduced in small portions while cooling to about 10–15° C. The reaction product obtained has a higher efficiency for protecting calcium soaps freshly formed from flocculation than the glucoside not treated with dimethyl sulfate.

24. Palmitoylmethylaminoethyl - glucoside is several times recrystallized from a benzenic solution. 1 part of the thus purified starting material is finely dispersed in 100 parts of acetone containing 2 per cent of hydrochloric acid gas and the dispersion shaken until the palmitoylmethylaminoethyl-glucoside has been dissolved in the main. The solution is then poured into the calculated amount of cold diluted sodium hydroxide solution and the thus obtained neutral solution is evaporated to dryness in a vacuum. The resulting reaction product dissolves clearly in water and has an improved washing and cleansing capacity when used for treating cotton

impaired by cacao spots, compared with the non-acetalized glucoside.

25. 2 parts of sodium hydroxide and 5 parts of dimethyl sulfate are added portion by portion to a solution of lauroyl-methylaminoethyl-glucoside, 10 per cent strong, while cooling. The clear frothing solution has a stronger capillar activity than the starting material.

26. 1 part of sodium hydroxide and 3 parts of benzoylchloride are added to a solution of 10 parts lauroyl-methylaminoethyl-arabino-
 10 side and the solution is shaken until the reaction has proceeded to completion. The reaction product is more capillar active than the untreated arabino-
 15 side.

27. 30 parts of a 33 per cent solution of methylaminoethyl glucoside according to Example 7 are heated with 5 parts of dodecyl bromide and 20 parts of alcohol for 4 hours, with stirring, to a temperature of 125 to 130°C. There is obtained a clear liquid which dissolves in water with
 20 frothing to give a clear solution.

28. 0.5 part of sodium hydroxide are added to 100 parts of a 10 percent solution of octadecylmethylaminoethyl-glucoside and ethylene oxide is introduced into this solution at room temperature until the increase of weight amounts to 30 parts. A clear, well frothing solution is obtained.

If wool is washed with a solution of the untreated octadecyl methylamino-glucoside at a pH value below 5 no washing effect is obtained at all. However by washing the wool with a solution of the said compound treated with ethylene oxide, the conditions being otherwise the same, a beautiful white wool is obtained.

29. 0.5 part of sodium hydroxide are added to 100 parts of a 10 per cent solution of hexadecylaminoethyl-glucoside and 25 to 30 parts of propylene oxide are introduced into this solution at room temperature. The reaction product dissolves clearly in water and exerts a good washing effect when used in the acid washing treatment of wool; the untreated hexadecylaminoethyl-glucoside having under the same conditions no washing effect at all.

30. 10 parts of octadecylaminoethyl-glucoside purified by repeated recrystallisation from benzene are heated with 2 parts of glycerol chlorohydrine and 1 part of finely powdered calcined sodium carbonate to a temperature of 70 to 80°C until the odour of glycerol chlorohydrine has practically disappeared. The reaction product has been found of high value for use in vat dyeing.

31. A purified octadecyl-aminoethyl-glucoside is heated with the equivalent amount of a chloroethyl ether of polyglycols or with polyglycerol chlorohydrin at a temperature of about 80°C while adding finely powdered calcined sodium carbonate. The resulting reaction product is more readily soluble in water than the untreated hexadecyl-aminoethyl-glucoside and is an improved leveling agent in vat dyeing.

32. Hexadecyl-aminoethyl-glucoside obtained from 6 parts of hexadecyl-amine and 10 parts of chloroethyl-glucoside (containing 62 per cent of the pure compound) 1.5 parts of calcined sodium carbonate and 30 parts of alcohol are heated in an autoclave with 10 additional parts of chloroethyl-glucoside (62 per cent) to a temperature of 140 to 145° C. The solution is separated by filtration after cooling from solid and oily matter, the alcohol is evaporated and the hexadecyl-aminoethyl-glucoside obtained is dissolved in wa-
 75

ter, whereby a clear solution is obtained. This solution may be used for washing operations in the whole range of pH values between 0 to 14; the monoglucoside being not capable to act in such manner.

33. 25 parts of a dispersion of 20 per cent of hexadecyl-methylaminoethyl-glucoside are treated with 1.8 parts of dimethyl sulfate and 0.3 parts of sodium carbonate, whereby quarternation of the nitrogen atom is effected. The reaction proceeds at ordinary temperature. The reaction product is more easily soluble than the untreated glucoside and forms solutions which are stable to the influence of alkaline reacting lyes.

34. 14 parts of sodium hydroxide are added to 100 parts of a 20 per cent dispersion of octadecylmethylaminoethyl-glucoside and shaken with 40 parts of dimethyl sulfate added repeatedly by small portions, while cooling to about 10-15° C. The solution obtained is neutralized and becomes clear when gently heated. It has a considerably improved equalizing action in dyeing operations with the aid of substantive dyes more particularly vat dyes than the glucoside before a treatment with dimethyl sulfate.

35. 4.5 parts of a purified hexadecyl-aminoethyl-glucoside are heated with reflux with 10 parts of benzene and 1.2 parts benzyl chloride until the odour of benzyl chloride has practically disappeared. After evaporation, preferably in a vacuum, a brownish mass is obtained, the solubility of which is less than that of the nonbenzylized glucoside.

36. A purified hexadecyl-aminoethyl-glucoside is heated with equimolecular amounts of chloroacetic acid and with finely powdered dried sodium carbonate to about 80° C until the reaction has proceeded to a substantial completion. The brownish melt obtained dissolves in water forming a clear solution. In contradistinction to the behavior of hexadecyl-aminoethyl-glucoside the modified compound has a considerable washing capacity when used for washing wool within a pH range of the solution between pH 7 to 11.

In the following claims I use the term "sugar" to include not only substantially pure pentoses and hexoses, aldoses and ketoses, aldoketoses and ketoaldoses, monosaccharoses, disaccharoses and other polysaccharoses e. g. starch and dextrin, and derivatives thereof, but also technical products rich in sugar for instance starch sugar or wood sugar.

Furthermore I use the term "low molecular alcohol" to define alcohols having 2 to 5 carbon atoms directly bound to each other; this definition therefore includes besides alcohols having an uninterrupted chain of not more than 5 C atoms also alcohols having more than one chain of carbon atoms linked by a hetero-atom such as —O— provided that each chain contains not more than 5 C atoms.

Furthermore I use the term "acid catalyser of the non-reversing type" to define acids or mixtures of acids and acid salts which have practically no or only a slight reversing action that is to say an unfavorable action leading to a formation of a considerable amount of condensed polysaccharoses. Examples of such acid catalysers are mentioned on page 2, column 1, lines 6 to 14. In contradistinction to "acid catalysers of the non reversing type" hydrochloric acid has a strong reversing action and is therefore not suitable in the present process.

AUGUST CHWALA.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR OBTAINING CRYSTALLINE MATERIALS FROM OILS

Karl Fehr and Wilhelm Schneider, Castrop-Rauxel 2, Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 8, 1939

This invention relates to a process for obtaining crystalline material from oils, and it has particular relation to the recovery of crystalline compounds from tar oils, particularly coal tar oils.

According to known methods, tars, for instance coal tar, are subjected to fractional distillation in order to obtain oil fractions rich in the crystalline compounds to be recovered. The recovery of these compounds is then effected by cooling said fractions to crystallization temperature, and separating the crystals formed from the bulk of the non crystallizable oils by filtering with suction or centrifuging. If sufficiently pure crystals cannot be obtained by these steps, the non crystallizable material must be separated from the crystals by squeezing off the oil, for instance in a high pressure press under a pressure up to 300 atm. This treatment, however, is not practicable or causes difficulties in some cases, owing to the high viscosity of the oily constituents or the smeary nature of the crystals. In such cases, the viscosity of the oil can be reduced by the addition of solvents, or the oil-containing crystals, after separation from the bulk of the oil, can be purified by dissolving and recrystallizing them by means of a suitable solvent. The use of solvents, however, causes an essential reduction in the yield of the crystals, particularly if the crystals are easily soluble. Moreover, losses of the solvent are unavoidable, and essentially raise the costs of the process.

It has now been found that the above mentioned drawbacks can be avoided, and crystals, which are essentially free from or poor in oil, can be obtained from oils, by proceeding as follows.

The oil fraction containing crystallizable compounds, for instance an oil obtained by fractional distillation of coal tar, is introduced into and mixed with a hot aqueous emulsion of an organic solvent, for said oil, the mixture obtained is cooled to crystallization temperature, and the crystals formed are separated from the emulsion. It has been found that the presence of water in said mixture causes slow crystallization of the crystallizable compounds contained in the oil. Moreover, the presence of water reduces the dissolution of the crystalline substance and losses caused by such dissolution. Finally, as the volume of the liquid is essentially increased by the addition of water, the crystals remain in a loose condition in the liquid, and can easily be separated from it.

The present invention may be used, for instance, for the recovery of crystalline substances

from oils which are obtained by fractional distillation of coal tar or coal tar oils and, owing to the formation of crystals, are semiliquid or solid at ordinary room temperatures, or consist of high-boiling substances which are highly viscous and not fluid at said temperatures. In carrying out the invention, the tar oil is heated until it forms an essentially homogeneous liquid, and is then introduced under stirring into a hot emulsion, which contains water and an organic solvent and preferably an emulsifying or wetting agent. The organic solvent is used for taking up the oily constituents of the tar oil, and may be a coal tar oil or another solvent, which is essentially not soluble in water, and can homogeneously be mixed with said oily constituents. Distillation products of coal tar, brown coal tar, carbonization tar or petroleum, may, for instance, be used. Other suitable solvents and mixtures of several solvents may also be used. The wetting or emulsifying agent influences the surface tension of the solvent and the oil to be treated and thus facilitates the thorough mixing of water, oil and crystalline substance. Soaps, for instance alkali soaps of colophony, naphthenic acid soaps, fatty acid soaps, salts of sulfo acids, or other wetting or emulsifying agents or their mixtures, may be used. Our present invention can also be carried out without employing such agents, as an intimate mixing of the above mentioned individual components may be effected by mechanical stirring alone. However, the use of emulsifying or wetting agents essentially facilitates the carrying out of the invention. The emulsifying or wetting agent may preferably be added to the solvent before mixing it with water, or may be formed by partial or complete saponification of saponifiable components contained in the solvent, which is then mixed and emulsified with the necessary amount of water. 20 parts of a tar oils solvent, to which a rosin soap has been added, may, for instance, be mixed and emulsified with 80 parts of water.

According to another embodiment of our invention a part of the solvent may be added to the oil containing the crystallizable substance to be recovered, and the other part of the solvent mixed and emulsified with water. Thereby, two different solvents may be used, one of which is used for diluting the oil containing the crystallizable substance to be recovered, and the other, to which an emulsifying or wetting agent may be added, for preparing the aqueous emulsion.

In carrying out the present invention, the crystals to be obtained are formed and separated

from the oil during cooling the mixture of starting material and aqueous emulsion of the solvent under stirring. The crystals thus formed can be obtained essentially free from oil, by separating them from the liquid mixture. They can be separated from the cooled mixture, for instance by filtering with suction or centrifuging, and can be washed with water in order to remove adhering particles of the emulsion. The residual oily parts of the starting material are taken up by the droplets of solvent which are finely distributed in the emulsion.

Example 1.—300 parts by weight of drained naphthalene are heated to 100°C and introduced under stirring into an emulsion obtained from 360 parts by weight of water and 90 parts by weight of a coal tar oil, which has a boiling range of 200° to 300° C and contains 20 parts by weight of sodium resin soap in solution. This emulsion is heated to 95°C before mixing it with the naphthalene containing material. The mixture is cooled under constant stirring to 30°C. Thereby, crystallization takes place, and the crystals are then separated from the liquid by filtering with suction. The crystals are then washed with water and centrifuged in order to separate them from water. Thereby 240 parts by weight of a naphthalene having a solidification point of 79.0 C are obtained. The naphthalene thus obtained contains only traces of water and corresponds in its quality to a hot-pressed naphthalene.

A change in the temperature, to which the mixture is cooled, for instance to 50°C, or 20°C or less, causes corresponding change in the yield and solidification point of naphthalene, in a manner similar to that which occurs in the customary pressing method by changing the pressure used and the duration of pressing.

Example 2.—300 parts by weight of a coal tar oil which boils between 293° and 309°C, and becomes clear when heated to 73°C are heated to 100°C, and treated, as described in Example 1, with an emulsion which has previously been heated to 95°C, obtained from 400 parts by weight of water and 100 parts by weight of a coal tar oil, which has a boiling range of 200° to 300°C and contains 20 parts by weight of sodium resin soap. By cooling the mixture under stirring to 25°C, filtering with suction, washing with water and centrifuging, 73.9 parts by weight of crystals are obtained. These crystals are free from water and contain only 6% of oil. This oil does not affect the further working up of these crystals which consist essentially of diphenylene-oxide, fluorene, and phenanthrene.

Instead of treating the above mentioned coal tar oil boiling between 293° and 309° C, the solid residue obtained by cooling this oil to ordinary room temperature and then subjecting it to filtering with suction, may also be treated according to our present invention. For instance, 200 parts by weight of such residue consisting of crystallized substances and oils are heated to 120° C and then mixed under stirring with an emulsion, which has previously been heated to 95°C, obtained from 200 parts by weight of water and 90 parts by weight of a coal tar oil which has a boiling range of 200–300° C and contains 20 parts by weight of sodium resin soap. After cooling and filtering with suction a mixture of crystals is obtained which after being washed with water is essentially free from oil. The crystals are freed from water by centrifuging and contain then about 3% of oil which is much less than the

oil contents of crystals obtained under similar conditions by pressing.

Example 3.—2000 parts by weight of a coal tar oil which boils between 310° and 330°C and becomes clear when heated to 120°C, are heated to 120°C and mixed under stirring with an emulsion which has previously been heated to 80°C obtained from 1600 parts by weight of water and 400 parts by weight of a tar oil which boils between 200° and 300°C and contains 20 parts by weight of sodium rosin soap in solution. The mixture obtained is cooled under stirring to 25° C and subjected to filtering with suction; the solid residue is washed with water and centrifuged. Thereby 1290 parts by weight of crystals are obtained which are free from water and contain 4–5% of oil, i. e. essentially less than contained in a product which is obtained under similar conditions by pressing.

Example 4.—300 parts by weight of a pyrene containing coal tar oil which boils between 382° and 394° C and becomes clear when heated to 76°C are diluted with 60 parts by weight of gas oil boiling between 220 and 360° C and heated to 100 C. The oil mixture thus obtained is introduced into a liquid of 100° C obtained from 100 parts by weight of liquid cresol soap, and 200 parts by weight of water. The liquid cresol soap may be obtained, for instance, by dissolving cresol in sodium-hydroxide or potassium hydroxide solution as described for example in pharmaceutical compendiums. The mixture is cooled under constant stirring to 25° C after which it is mixed by stirring with a further amount of 200 parts by weight of water. The crystals formed are separated from the liquid by filtering with suction and washed with about 500 parts by weight of water. Thereby 165.9 parts by weight of crystals are obtained. The crystals contain only 2.5% of oil and traces of water.

Example 5.—300 parts by weight of the coal tar oil used in accordance with Example 4, are mixed with 60 parts by weight of a coal tar oil which boils between 180° and 210° C. The mixture is heated to 100° C and introduced under thorough stirring into a 100° C hot solution of 75 parts by weight of sodium soap of naphthenic acid and 75 parts by weight of water. The mixture is cooled under stirring to 35 C; it is then mixed by stirring with a further amount of 300 parts by weight of water. By further cooling to 25° C, filtering with suction and washing with water, 152.1 parts by weight of crystals are obtained which are free from water and contain only 1% of oil.

The process of our present invention can also be used for obtaining crystallizable substances from other oils essentially in the same manner as described in the above examples.

The amounts of the solvent, wetting or emulsifying agents and of water, to be used depend on the properties of the starting material which contains the crystallizable compounds to be obtained. The carrying out of the present process requires the use of sufficient amounts of the substances to be added. Sufficient water should be added in order to obtain a mixture which can be stirred thoroughly even at lower temperatures, and sufficient solvent should be present for taking up the oily portions contained in the mixture. We prefer to use for preparing the emulsion 20–30 parts by weight of a solvent containing a wetting or emulsifying agent, and 70 to 80 parts by weight of water. For carrying out the process of our present invention we also prefer

to use an amount of this emulsion, which, after mixing with the oil to be treated, will still be of the oil-in-water type. This facilitates the washing of the separated crystals with water.

Owing to the presence of water, the above described emulsions cannot be heated to temperatures over 100° C. It is, therefore, not advisable to heat the oils to be treated to temperatures essentially higher than those disclosed in the above examples. It is, however, advantageous to reach the temperature of 100°C during mixing the oil with the emulsion in order to obtain a slow crystallization. The cooling may be performed in any suitable manner with or without artificial cooling of the stirring apparatus. The slower the cooling is performed, the better the crystals can develop. The separation of crystals from the liquid can be carried out in any suitable device, for instance by means of a suction filter or

by treating the mixture of crystals and liquid in a centrifuge. The washing of the crystals can take place, for instance in a suction filter or in a centrifuge.

In our present specification and claims "crystallization temperatures" it is to be understood are those at which the crystallizable substances to be obtained from the oils separate from said oils in the form of crystals, whereas the oils and solvents used, and the water present in the emulsion, still remain liquid. The term "solvent" used in the present specification and claims denotes liquids which are essentially not soluble in water and can be mixed homogeneously with the oils from which the crystallizable substances have been separated.

KARL FEHR.
WILHELM SCHNEIDER.



ALIEN PROPERTY CUSTODIAN

METHOD FOR THE MANUFACTURE OF
WRITING-MASSSES

Heinrich Schwappacher, Stein, near Nuremberg,
Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 26, 1939

The invention refers to the manufacture of writing-masses from writing-substance, filling-materials, and binding-materials.

The object of the invention is making writing-masses e. g. mines for pencils which are insensitive to moistness.

According to the invention this object is attained by using for the manufacture of pencil-mines binding-materials which are originally soluble in water, but which by heat treatment are transformed into insoluble state without their binding capacity being impaired.

As binding-materials of this kind artificial resins soluble in water e. g. condensation products soluble in water from phenol and formaldehyde or condensation products from urea and formaldehyde are used. These artificial resins are made insoluble by heat treatment.

As binding materials in the spirit of the invention also aqueous solutions of two or several artificial resins may be used. Such solutions combine into insoluble artificial resins under the action of heat.

Furthermore products of condensation soluble in water from phenol and formaldehyde or condensation products soluble in water from urea and formaldehyde may be used and rendered insoluble by adding hardening agents under heat treatment.

Finally, apart from the binding materials consisting of artificial resin, also other binding materials soluble in water e. g. tragacanth may be used.

In carrying the invention into effect, the following mixtures of substances are used by way of example:

<i>Example I</i>		Parts
Methylene blue.....		28
Graphite		45
Condensation product soluble in water from phenol and formaldehyde (resol).....		24
Softening material.....		3
		100

<i>Example II</i>		Parts
Eosin		28
5 Kaolin		35
Stearate of calcium		10
Condensation product soluble in water from urea and formaldehyde (e. g. caurit) in powder-form and in solution.....		22
10 Tragacanth		5
		100

<i>Example III</i>		Parts
15 Methylene blue		28
Kaolin.....		20
Talc		15
20 Stearate of calcium.....		10
Dimethylol urea plus hardening agent (formic acid ester)		22
Tragacanth		5
		100

From the mixture of substances according to Examples I or II or III a paste-like mass is formed under addition of water. This mass which is plastic, is then pressed into mines in the way usually employed in manufacturing pencil-mines. The finished mines are so insensitive to moisture that they may be boiled in water without softening.

According to the invention writing-, drawing-, copying- and colour-mines of any kind may be made, as well as rod-shaped writing-implements such as drawing- or marking-chalk.

HEINRICH SCHWAPPACHER.

ALIEN PROPERTY CUSTODIAN

DICHLOROBUTENES AND A PROCESS OF PREPARING THEM

Walter Schmidt, Frankfurt am Main, Germany;
vested in the Alien Property Custodian

Application filed July 29, 1939

The present invention relates to dichlorobutenes and to a process of preparing them.

It is known that dichlorobutene is obtained by adding chlorine in a quantity insufficient for complete chlorination to butadiene in presence of a solvent. It is necessary in this case to use a relatively large quantity of the solvent and to work with a large excess of butadiene in order to prevent further chlorination of the first formed dichlorobutenes into the tetrachlorobutane from becoming the preponderating change. The yield per unit of space and time is, therefore, very moderate and the hydrogen chloride, formed by the substitution-chlorination which always occurs as by-reaction is present in the solution and, by addition, leads in its turn to undesired by-products. Finally, the distillation which is necessary when the reaction has proceeded for a comparatively short time in order to avoid high concentration of the chlorination products renders the process expensive in view of the large amount of solvents which are carried over and unavoidable losses in distillation. It has been proposed to use liquefied butadiene as a solvent, but this necessitates the use of a large excess and the application of very low temperatures, for instance, -75°C ; even then it is not possible to avoid the substitution-chlorination or the subsequent chlorination with formation of tetrachlorobutane.

Now, I have found that the chlorination of butadienes with formation of dichlorobutene may be performed in an economic and technically simple way by causing gaseous butadiene to react with gaseous chloride in the absence of a solvent but in the presence of a substance which is gaseous during the reaction and insensitive towards chloride and butadiene, such as, for instance, nitrogen and the noble gases, halogenated hydrocarbons, carbon dioxide and the like. In this manner the costs for working up the product are considerably diminished in view of the omission of the large quantity of solvent. Furthermore, the dichlorobutene first formed by the circulation of the gas is quickly removed from the reaction zone and thus from further chlorination; the direct chlorination to a higher stage is avoided since the chlorine is much diluted by the gas; a good yield of dichlorobutene is thus obtained.

As diagrammatically illustrated in the accompanying drawing, the reaction may, for instance, be performed in a cooling device which may be charged partially or entirely with filling material, an inlet tube for the chlorine extending into this reaction chamber which tube may have the form

of a nozzle. Butadiene is circulated by means of a pump and caused to react with chlorine diluted with gas; the product of reaction is removed and a quantity of waste gas corresponding with the gas used for diluting the chlorine is continuously withdrawn. The circulating gas becomes mixed with a small proportion of hydrogen chloride which may readily be removed from the gas. The exit gas is freed from small quantities of butadiene and HCl and after cooling or washing may be used further for diluting chlorine so that the working is continuous and economic.

The volume of the inert diluent suitably is equivalent to the volume of the chlorine; there may, however, also be applied considerably larger amounts, for instance, fifty times the volume. The upper limit of the amount to be applied merely depends upon economical considerations.

The proportion of the chlorine used is preferably at most 1 mol per mol of the butadiene; advantageously, there are used not less than 0.75 mol of chlorine per 1 mol of the butadiene.

The reaction may be performed at temperatures of about -20°C to about $+20^{\circ}\text{C}$. The higher the temperatures applied are, the larger are the amounts of the gaseous diluent to be added.

The following examples serve to illustrate the invention but they are not intended to limit it thereto:

1. Referring to the accompanying diagram, an inlet tube for introducing chlorine having a diameter of 1 cm extends about 15 cm into the cooling zone at the upper end of a cooling tube 1 of 135 cm length and a diameter of 3 cm surrounded by a cooling jacket. To a depth of about 10 cm the lower cooling zone is charged with filter rings. A separating chamber 2 for the liquid is connected with a second cooler 3 provided also with a separating chamber 4 for the liquid and with a cock 5 for the waste gas. A pump 6 causes the butadiene to circulate in the apparatus. From the container 7 chlorine is discharged, from 8 nitrogen and from 9 butadiene. 10, 11, 12 and 13 are devices for measuring the speed of the gases.

The temperature in the cooler is maintained at about -5 to $+10^{\circ}\text{C}$ by means of a cooling liquor in its jacket so that butadiene at a speed of circulation of even 2000 liters per hour does not liquify. A mixture of 9.5 liters of chlorine and 100 liters of nitrogen is introduced per hour through the chlorine-inlet tube and at the same time 10 liters of butadiene per hour are introduced at the upper end of the first cooling tube. The liquid chlorination product obtained collects in the two separating chambers; the quantity of

gas introduced is such that a pressure of 5 cm of mercury above atmospheric pressure is maintained in the apparatus. The exit gas contains traces of hydrogen chloride and small quantities of butadiene; it is freed therefrom and may then be used again for diluting the chlorine. After 4½ hours 250 grams of liquid product will have been collected which, when fractionated, yields besides small quantities of butadiene

	Per cent	
1:2-dichlorobutene-3, boiling at 42°C-44°C		
under a pressure of 40 mm-----	34.3	
1:4-dichlorobutene-2, boiling at 61°C-63°C		
under a pressure of 2 mm-----	39.7	
Chlorination products of higher boiling		
point, mainly tetrachlorobutene-----	23.1	15

2. The operation is the same as in example 1, except for the fact that the chlorine is not diluted with nitrogen but with gaseous difluorodichloromethane at a rate of 50 liters per hour. After 5 hours 280 grams of liquid will have been collected which contain:

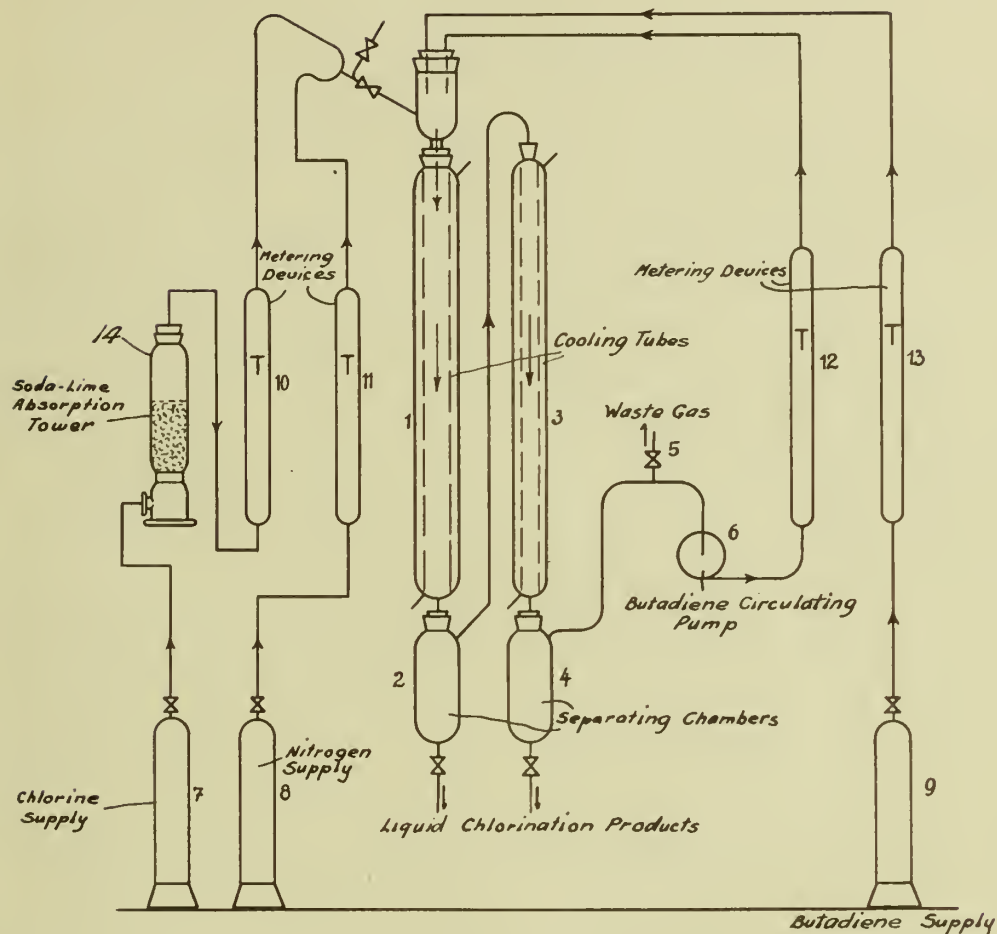
	Per cent
1:2-dichlorobutene-3 -----	28.5
1:4-dichlorobutene-2 -----	36.6
Chlorination products of higher boiling	
point -----	29.7

WALTER SCHMIDT.

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DICHLOROBUTENES AND A PROCESS
OF PREPARING THEM
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Walter Schmidt
INVENTOR

BY *Walter and Joslin*
HIS ATTORNEYS



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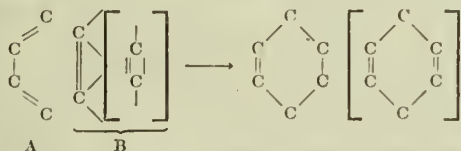
CONDENSATION PRODUCTS

Kurt Alder and Erwin Windemuth; Cologne, Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 29, 1939

The present invention relates to new condensation products and to the process of preparing the same.

The so-called "diene-synthesis" resides in the addition of compounds containing two conjugated C=C double linkages with such compounds containing an ethylene or acetylene group where- in the said unsaturated linkage is likewise con- jugated with another double bond. In general, the "diene-synthesis" proceeds in the following manner:



it being to be understood that in the reaction component designated by symbol B the unsaturated linkage is activated by another double bond as stated above. Examples for compounds of type B are 1,3-dienes, λ,β -unsaturated aldehydes, ketones, carboxylic acids and carboxylic acid nitriles.

The present invention is based on the observation that the "diene-synthesis" is not restricted to the situation as defined above. We have found that compounds containing non-conjugated C—C double linkages or threefold linkages and containing polar radicals, said polar radicals being separated from the said double or threefold linkages by one carbon atom, are likewise capable of forming addition products of the character described, if reacted upon with compounds containing two conjugated C=C double linkages. The term "polar radicals" comprises groups of the following type: hydroxyl, amino, aryl, halogen, carboxyl (including esterified carboxyl) nitrile, —OOC.R (R being an organic radical), and —N=C=S. Reference is made in this connection to the textbook "Stereochemie" by K. L. Wolf and O. Fuchs (1933). Examples for compounds containing 2 conjugated C=C double linkages are those commonly employed in the diene-synthesis, such as butadiene-1,3, isoprene, 2,3-dimethylbutadiene-1,3, cyclopentadiene, cyclohexadiene and anthracene. Particular importance is attached to the use of compounds of the following formula:



wherein X stands for one of the above polar groups.

The reaction is performed by simply heating the mixture of the starting materials, preferably in a closed vessel. As a matter of fact care must be taken that the reaction is performed under such conditions as to prevent any substantial polymerization. To this end, polymerization inhibitors such as hydroquinone, pyrogallol and the like may be added to the reaction mixture, particularly in case of working with butadiene-1,3, isoprene and 2,3-dimethylbutadiene. As stated above, the reaction is performed at an elevated temperature, it being impossible to give definite lower and upper limits, since the optimum reaction conditions depend on the nature of the starting materials and on the tendency of the butadienes and the like to form dimeric products. In general, the dimerization process occurs more slowly than the addition of the 2 reaction components. On the other hand, some of the dimeric products may be split up into the monomeric products at a high temperature, whereas the addition products formed by the interaction of the 2 reaction components are stable at such temperatures. Thus, in case of cyclopentadiene the reaction is preferable performed at 180° C as at this temperature the dimerics are split up so that the addition process is nearly quantitative. Other dienes such as anthracene do not show any tendency to form dimerics at the usual reaction temperature.

The new products which are obtainable in accordance with our invention may be defined as products of the addition of one to two molecules of a compound containing 2 conjugated C=C double linkages and one molecule of the other reaction component.

The following examples illustrate the present invention without, however, restricting it thereto, the parts being by weight.

Example 1

22 parts of allyl alcohol and 21 parts of cyclopentadiene are heated in an autoclave for 11 hours to 175–180° C. On distilling in vacuo there is obtained in a good yield the addition product of the components at 92–94° C under 13 mm pressure. It represents a colorless oil of a slightly peppermint-like smell.

On subjecting the reaction product to catalytic hydrogenation it takes up two hydrogen atoms and thereby being converted into the 2,5-endomethylenhexahydro-benzylalcohol (boiling point 95–96° C at 13 mm pressure). The acid phthalate has the melting point 111–112° C

Example 2

30 parts of salicylic acid-allylester, 10 parts of cyclopentadiene and some hydroquinone are heated in an autoclave for 11 hours to 175–180° C. On distilling in vacuo the reaction product, there is obtained the addition product of the components in form of a colorless oil at 185–186° C under 11 mm pressure.

Upon the action of phenyl-azide the reaction product is converted into a crystalline hydrotriazole of the melting point 154° C.

Example 3

10 parts of allyl alcohol (containing about 30% of water), 5 parts of anthracene and 25 parts of benzene are heated in an autoclave for 12 hours to 210° C. After distilling off the solvent there remains the addition product of the components which, after recrystallizing from high-boiling ligroine, yields colorless crystals of the melting point 112° C. The acetyl compound of the addition product melts at 122° C.

Example 4

30 parts of crotyl alcohol and 50 parts of cyclopentadiene are heated in an autoclave for 12 hours to 170–180° C. In vacuo the addition product of the components distills over at 105–110° C. When acetylating the same with acetic acid anhydride, hydrogenating and saponifying there is obtained the 2.5-endomethylen-6-methyl-hexahydrobenzylalcohol of the boiling point 103–104° C at 12 mm pressure. The acid phthalate has the melting point 98° C.

Example 5

14 parts of allylisothiocyanate and 13 parts of 2.3-dimethyl-butadiene are heated in an autoclave for 12 hours to 145–155° C. On distilling the reaction product in vacuo there is obtained the addition product of the components in form of an oil with an intensively garlic-like smell, the melting point being 137–138° C under 12 mm pressure.

Example 6

10 parts of allylisothiocyanate and 6.5 parts of cyclopentadiene are heated in an autoclave for 12 hours to 145–155° C. On distilling the reaction mixture in vacuo there is obtained the addition product of the components in form of a clear oil, the boiling point being 121–123° C under 12 mm pressure. Upon the action of phenyl-azide the reaction product yields a crystalline hydrotriazole of the melting point 116–117° C.

Example 7

10 parts of allylchloride, 5 parts of anthracene and 25 parts of benzene are heated in an autoclave for 13 hours to 220° C. After recrystallizing from alcohol the addition product yields colorless needles of the melting point 115–116° C.

Example 8

100 parts of allylchloride and 50 parts of cyclopentadiene are heated in an autoclave for 8 hours to 170–180°C. After distilling off the excess allylchloride the reaction liquid is distilled in vacuo. Thereby the addition product of the components is obtained in form of a colorless oil in an excellent yield, the boiling point being 54–56° C under 11 mm pressure.

Upon the action of phenylazide the addition product yields a crystalline hydrotriazole of the melting point 133–134° C.

Example 9

56 parts of allyl-bromide and 27 parts of cyclopentadiene are heated in an autoclave for 8 hours to 170° C. There is obtained the addition product of the components in a very good yield at 75–77° C under 13 mm pressure.

Example 10

25 parts of allyl iodide and 10 parts of cyclopentadiene are heated in an autoclave for 5 hours to 100–105° C. On distilling in vacuo there is obtained the addition product of the components in form of an oil of the boiling point 107–109° C under 15 mm pressure.

Example 11

30 parts of allylamine and 28 parts of cyclopentadiene are heated in an autoclave for 8 hours to 170° C. The addition product boils at 61–62° C under 12 mm pressure.

Upon subjecting the addition product in form of its hydrochloride to a catalytic hydrogenation two hydrogen atoms are taken up with the formation of the hydro-chloride of the 2.5-endomethylenehexahydrobenzylamine. The urea derivative thereof has the melting point 124° C.

Example 12

35 parts of vinyl-acetic acid and 24 parts of cyclopentadiene are heated in an autoclave for 8 hours to 175–180° C. On distilling in vacuo there is obtained the addition product of the components in form of a colorless oil of the boiling point 142–144° C under 13 mm pressure. For purifying the crude acid is dissolved in a sodium carbonate-solution and the solution is shaken with ether in order to remove some neutral reacting constituents; from the solution of the sodium salt the pure reaction product, i. e. the 2.5-endomethylen- Δ^3 -tetrahydro-phenylacetic acid is obtained in form of a colorless oil of the boiling point 137–139° C under 12 mm pressure.

When hydrogenating this acid, the saturated 2.5-endomethylen-hexahydro-phenylacetic acid is formed, the anilide of which melts at 138° C.

Example 13

15 parts of allylcyanide and 12 parts of cyclopentadiene are heated in an autoclave for 12 hours to 170–180° C. On distilling off the reaction product in vacuo there is obtained the addition product at 89–93° C under 11 mm pressure. It represents a colorless oil with a strongly clove oil-like smell. The addition product contains the components in the molecular proportion and yields with phenylazide a crystalline hydrotriazole melting point: 174–175° C.

Besides this normal addition product there is obtained a second one in a small amount which contains cyclopentadiene and allylcyanide in the relative proportion 2:1, boiling point being 165° C under 11 mm pressure. With phenylazide there is obtained a hydrotriazole of the melting point 202–203° C.

Example 14

67 parts of eugenole and 27 parts of cyclopentadiene are heated in an autoclave for 8 hours to 170–180° C. On distilling in vacuo there is obtained besides some dicyclopentadiene and unchanged starting materials the addition product in form of a colorless oil of the boiling point 138–142° C at 0.1 mm pressure, the melting point being 35° C.

With phenylazide there is obtained a hydro-triazole of the melting point 210–211° C.

Example 15

10 parts of buten-2-diole-1,4, 10 parts of cyclopentadiene and 20 parts of dioxane are heated in an autoclave for 8 hours to 175–180° C. On distilling in vacuo there is obtained in a good yield besides some di- and tricyclopentadiene the addition product of the components in form of a colorless oil (boiling point 165–170° C under 13 mm pressure) which directly crystallizes.

Example 16

10 parts of 2-methyl-butin-3-ol-1 and 10 parts of cyclopentadiene are heated in an autoclave for 8 hours to 180–185° C. On distilling in vacuo there is obtained besides some methyl-butin-ol and dicyclopentadiene the addition product of the components in form of a colorless oil (boiling point 77–83° C under 13 mm pressure) with an eucalyptus-like smell.

KURT ALDER.
ERWIN WINDEMUTH.



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HEXAESTERS OF TETRAPHOSPHORIC ACID

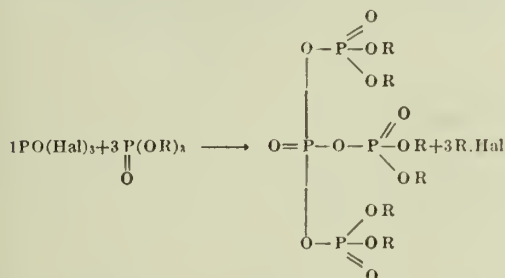
Gerhard Schrader, Leverkusen I. G.-Werk, Germany; vested in the Alien Property Custodian

No Drawing. Application filed August 1, 1939

This invention relates to the manufacture of hexaesters of tetraphosphoric acid.

Tetraphosphoric acid esters have hitherto not been known.

It has been made the surprising discovery that the hexaesters of tetraphosphoric acid can be easily prepared by causing phosphorous oxyhalogenides to react with neutral phosphoric acid esters, preferably at elevated temperature. The reaction scheme is as follows



R being an organic radical, 1 carbon atom of which is directly linked to the oxygen atom.

As neutral phosphoric acid esters above all the triethyl-, tributyl- and the tri-(chloroethyl)-phosphate respectively come into consideration which are technically used as softeners. Other suitable esters are, for instance, tripropyltrimethoxyethyl- or tricyclohexylphosphate respectively.

As phosphorous oxyhalogenides, for instance, phosphorous oxychloride or phosphorous oxybromide can be used.

For carrying out the reaction it is not necessary to use a solvent.

The reaction is suitably performed at temperatures between 130 and 150° C and proceeds nearly quantitatively.

The products according to the invention represent water-soluble oils which have a glycerine-like consistency. They may be used, for instance, as lubricants or softeners.

The following example illustrates the invention without, however, restricting it thereto:

Example

182 gs of triethylphosphate are heated while stirring under reflux so that the temperature of the liquid is about 150° C. Within half an hour 53 gs (1/3 mol) of phosphorous oxychloride are added drop by drop. After the addition of phosphorous oxychloride the temperature is kept still half an hour at 150° C; hereupon the mixture is cooled. 164 gs of the tetraphosphoric acid hexaethylester are thus obtained. Yield: 96%.

In a similar manner the following substances may be prepared:

tetraphosphoric-acid-hexa-n-butylester
tetraphosphoric-acid-β-chloroethylester
tetraphosphoric-acid-hexa-n-dodecylester
tetraphosphoric-acid-hexa-n-propylester
tetraphosphoric-acid-β-methoxyethylester
tetraphosphoric-acid-cyclohexylester.

All the last-named substances represent oils with glycerine-like consistency.

GERHARD SCHRADER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF BUTADIENE

Giulio Natta, Milano, Italy; vested in the Alien Property Custodian

No Drawing. Application filed August 11, 1939

The synthesis of butadiene, C_4H_6 , has attained today a remarkable importance owing to its use in the manufacture of synthetic rubber.

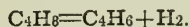
The processes heretofore employed for the manufacture of butadiene starting from alcohol and aldehyde offer, however, many inconveniences, owing to the low industrial yield obtainable, the high cost of the raw materials and the difficulty of obtaining butadiene in a very pure state.

Attempts for the manufacture of butadiene from a less expensive raw material, e. g. from butylenes C_4H_8 , obtained as by-products from petroleum cracking, had not heretofore given industrially interesting results, owing to difficulties in the separation of butylenes from butadiene as a consequence of the low yields obtained and owing to the poisoning of the catalysts after a short time of working.

We have now found a continuous process whereby it is possible to obtain a high yield in butadiene from butylenes and particularly from alpha-butylene, completely avoiding the above mentioned inconveniences. In what follows the expression "butylene" will mean chiefly alpha- or $\Delta 1-2$ -butylene, but also beta- or $\Delta 2-3$ -butylene in both its cis- and trans-forms, and/or mixings of two or of all these of the above named.

The mentioned process consists in the catalytic dehydrogenation of butylene on dehydrogenating catalysts, e. g. on nickel deposited on a suitable support, in the presence of a substance which by its presence promotes the dissociation of butylene in hydrogen and butadiene and prevents the deposition of the elementary carbon and/or of other organic substances on the catalyst:

We have found that it is possible to carry out said process by mixing with butylene, before entering the reaction oven, a given quantity of carbon dioxide, the presence of which promotes the reaction:



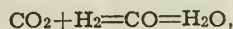
This effect is due to many reasons: first because the carbon dioxide causes a diminution of the partial pressure of the single components which take part in the reaction and it is known that a diminution of pressure favours the reactions which take place with an increase of volume. Further the carbon dioxide helps to prevent the formation of free carbon which, if deposited on the catalyst, would quickly poison it by reacting with it forming carbon monoxide.

The influence of carbon dioxide is, however, much greater than that which could be foreseen on the ground of the above considerations.

In fact, an addition of steam would also be sufficient to obtain from said points of view an effect similar to that given by carbon dioxide, but this is practically not the case. This is due, partially at least, to the fact that carbon dioxide takes part in the reaction either reacting directly with butylene according to the equation:



or through its reaction with hydrogen,



thus promoting the reaction of dehydrogenation of butylene.

While the kinetic mechanism of reaction is not yet fully explained, the remarkably advantageous action of carbon dioxide can be explained only by admitting its activating action on the dehydrogenating catalyst, or its participation to an intermediate reaction which is kinetically more speedy.

As catalysts, besides nickel, may be used other elements belonging to the same group and possessing a dehydrogenating activity. Should it be desired to avoid the use of more costly metals, good results may be obtained by the use of catalysts obtained by the dispersion upon porous supports, like alumin or silica or better bentonite, of finely divided nickel obtained, e. g. by reduction of reducible nickel salts as basic carbonate, oxalate, hydroxide, and the like, which have been precipitated on the support itself. The temperature of dehydrogenation may vary within broad limits but the best results are obtained at temperatures ranging between $500^\circ + 700^\circ C$ and preferably between $500^\circ + 600^\circ C$.

For instance a mixing consisting of equal volumes of alpha-butylene and carbon dioxide is led at $500^\circ - 600^\circ C$ through a catalyst layer consisting of bentonite on which 5% of nickel is deposited, and, after separation of carbon dioxide and of the gases more difficult to condense, yields a mixing containing about equal volumes of butylene and butadiene and even, when the speed of passage on the catalyst is low, more butadiene than butylene.

The carbon dioxide, separated by means of suitable solvents, may be returned in circulation while the separation of butylene and butadiene may be obtained by condensation.

The separation of butylene from butadiene may be carried out by fractionating solution by means of suitable solvents following known methods; the separated butylene may be returned in circulation and converted into butadiene. It is

also possible to obtain by a single operation a yield so high, to render it possible the separation of butylene from the formed butadiene, by polymerization of butadiene e. g. with sodium, thus directly obtaining synthetic rubber of good quality.

By thus operating and by returning in circulation the unaltered butylene, it has been possible to obtain yields in butadiene which in the total are higher than 80% of the butylene employed.

The above mentioned process may be applied not only in the case of butylene coming from cracking gases, but also in the case of butylene, or mixings of butylenes, obtained by other ways e. g. butylene obtained by dehydration of butyl-alcohol, also butylene obtained as a by-product in the manufacture of butadiene obtained by processes based on the catalytic decomposition of mixings of alcohol and acetic aldehyde on alumina or other catalysts.

In fact, following the last mentioned process a quantity of butylene which corresponds to 20+30% of the butadiene produced, is obtained as a by product.

The recovering of said butylene and its transformation in butadiene by the process herein-before disclosed, allows to increase by 20% the total output of butadiene without increasing the consumption of raw materials, alcohol and aldehyde.

It is further possible to use alpha-butylene obtained from normal butyl alcohol by a reaction which may be carried out with practically quantitative yields i. e., by dehydration of said normal butyl alcohol on catalysts mainly consisting of alumina or of caolin. The butylalcohol may have been obtained by hydrogenation of aldol.

Besides alpha-butylene, beta-butylene or mixings of both may be used, because during the dehydrogenation of beta-butylene a migration of the pre-existing double bond takes place.

5 The dehydrogenation reaction of the butylenes is endothermal and the heat of reaction must be supplied from the outside by heating the reaction chamber with hot gases or by indirect or direct heating of the catalyst or of the reacting gases by means of electric resistences. As the reaction is reversible, it is useful that the reaction gases leave the catalyst at the highest temperature of the cycle and be at once cooled down.

15 It is also possible, in order to avoid the need of addition of heat from the outside which is expensive owing to the high reaction temperature, to carry out a partial combustion inside the reaction chamber of the hydrogen coming from the dehydrogenation of butylene. For this purpose it is sufficient to mix carbon dioxide with the small quantity of oxygen, or air required to develop by burning a quantity of heat capable to balance the heat absorbed by the reaction of dehydrogenation and to bring the reacting gases to the reaction temperature.

25 In order to diminish the latter mentioned amount of heat it is useful to pre-heat the gases which enter in the reaction chamber, by utilising the heat possessed by the gases issuing from the reaction chamber itself. In this case small quantities of oxygen or air, substantially lower than the lowest limit of explosion of the mixing, are sufficient to maintain stationary the temperature of the catalyst without addition of heat from the outside.

GIULIO NATTA.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF OLEFINE OXIDES

Gerardus Hendricus Visser, Amsterdam, The Netherlands; vested in the Alien Property Custodian

No Drawing. Application filed August 14, 1939

This invention relates to a process for the production of olefine oxides which comprises reacting an olefine with an oxygen-containing gas in the presence of a highly active silver metal catalyst prepared by subjecting silver and/or silver compounds while in an aqueous medium to the action of nascent hydrogen.

An object of the present invention is to provide an improved process for converting olefines to olefine oxides by means of an extremely active silver metal catalyst. A further object of the invention resides in a practical, economical and broadly applicable method of effecting the catalytic oxidation of olefines to olefine oxides.

By oxidizing olefines in the presence of the highly active silver metal catalysts prepared in accordance with the invention, high yields of the valuable olefine oxides may be obtained. Although part of the olefines are oxidized in the process to incidental by-products including carbon dioxide, water and aldehydes, the use of my silver metal catalyst permits a high yield of the desired olefine oxide to be obtained and provides a highly desirable method for commercially manufacturing the olefine oxides.

Normally gaseous or readily volatile unsaturated organic compounds such as ethylene, propylene, the butylenes, the amylenes and their homologues and suitable substitution products are preferably employed in the process. A substantially pure olefine may be used or, if desired, a mixture of several olefines is suitable. Furthermore, various diluents may be used with the olefines such as paraffins. Being able to use mixtures of an olefine or olefines with paraffin hydrocarbons is very desirable since fractions containing these constituents may be used without separation therefrom of the paraffins; these fractions being readily obtainable from thermal and catalytic cracking of petroleum and shale oils, destructive distillation of coal, cracking of synthetic hydrocarbon oils and the like. It may be desirable to use other diluents with the olefines such as comparatively inactive gases like carbon dioxide, hydrogen, nitrogen, steam, etc.

The oxygen-containing gas used in the process may be substantially pure oxygen or it may contain one or more other gases such as nitrogen, hydrogen, carbon dioxide, steam and the like. Air is a preferred oxygen-containing gas for use in the process, although other gas mixtures containing oxygen may be especially desirable under some conditions.

The high yields obtained by the process are believed to be due to the very active catalyst em-

ployed and the activity of the catalyst appears to be due to the novel method of preparing the silver. Heretofore silver catalysts have been prepared by several different methods. One commonly used method consists in impregnating an inert spacing material with an aqueous solution of a silver salt, heating the resulting mass under controlled conditions to drive off water and the acid radical with which the metal is combined to produce the oxide of the metal, air being present if necessary to the formation of the oxide, and reducing the oxide at suitable temperatures in the presence of a reducing gas. Another method in use for the preparation of silver metal catalysts consists in thermally decomposing, preferably in a reducing or inert atmosphere, an organic silver compound, for example, a silver salt of a carboxylic acid. Finely divided silver metal catalysts are also prepared, principally for use in liquid phase reactions, by dissolving or suspending decomposable silver compounds in inert liquid media or in liquids intended for subsequent reaction and decomposing the silver compound in situ by the application of heat usually with the passage of hydrogen through the liquid in which the resulting metallic silver is deposited.

Some of the silver catalysts prepared in accordance with the prior art methods under properly controlled temperature conditions have a certain degree of effectiveness in accelerating the normal rate of many chemical reactions, but none of a great number tested have the effectiveness of the silver catalysts of the present invention in accelerating the rate of oxidation reactions. The silver metal catalysts prepared in accordance with the process of the invention are particularly effective in effecting the oxidation of ethylene to ethylene oxide. Their use permits the attainment of better yields, while operating at lower temperatures and thereby decreasing losses due to side reactions, than can be obtained with silver catalysts prepared by the known methods.

In accordance with the present invention silver metal catalysts are prepared by subjecting silver and/or silver compounds while in an aqueous medium to the action of nascent hydrogen. The nascent hydrogen may be generated in the liquid medium in which the silver metal catalyst is being prepared and/or it may be introduced into said medium, during the preparation of the silver metal, from a suitable outside source.

Nascent hydrogen suitable for use in the execution of the process of the invention may be prepared in a variety of manners. For example, nascent hydrogen may be prepared by electroly-

sis, by dissolving non-noble metals in aqueous media, by effecting electrical discharges in a hydrogen atmosphere, by effecting the thermal decomposition of ordinary hydrogen, etc. In the execution of the process of the invention, any one or any combination of the above and other means may be employed to furnish the nascent hydrogen prior to or during its use. For the attainment of the best results, the nascent hydrogen is preferably used as soon as practicable after its preparation. For this reason, it is desirable, in many cases, to prepare the catalyst in such a manner and under such conditions that, in the same media and at the same time, nascent hydrogen is generated and acts on the silver metal during and after its formation.

The catalyst may, for example, be prepared in the desired form in aqueous medium and while being subjected to the action of nascent hydrogen generated in situ by resorting to methods of electrolysis. A variety of conventional electrolysis cells may be used, and the active silver metal catalysts prepared by electrolytic reduction of a wide variety of inorganic and/or organic silver compounds. In one embodiment of the invention, both the anode and the cathode are silver. The silver electrodes are placed in a cell of suitable size and containing the required amount of electrolyte, and the current applied. Silver metal, which has been subjected to the action of nascent hydrogen formed in the cell, deposits on the cathode in the form of a spongy, grey precipitate. The precipitated silver metal can from time to time be scraped from the cathode and removed from the cell without interrupting the operation. During the electrolysis, it is, in general, advantageous to keep the electrolyte in the cell in motion by mechanical stirring or other suitable means. The electrolysis is conveniently effected at about room temperature, but higher or lower temperatures may be used when necessary or desirable.

The electrolyte used comprises water to which has been added in the desired amount an acid, salt or base which ionizes and makes the aqueous medium a conductor. If desired, the electrolyte may be an aqueous solution of a silver salt, such as silver nitrate. Other conveniently employed electrolytes are the aqueous solutions of the alkali metal salts. The current density applied may vary considerably. In general, current densities of from about 0.75 to about 3 amperes per square decimeter are suitable.

In removing the electrolytically reduced silver metal catalyst from the cell and preparing it for subsequent use by washing and drying, it is desirable to preserve the activity of the catalyst by avoiding contact with the air as much as possible. This may be done by effecting such operations in an inert atmosphere, for example, in an atmosphere of nitrogen or hydrogen.

Another convenient method of executing the process of the invention to obtain a highly active silver metal catalyst comprises reducing a silver compound in an aqueous medium by means of nascent hydrogen generated in said aqueous medium by dissolving therein a metal less noble than silver. The aqueous medium in which the reduction of the dissolved or suspended inorganic or organic silver compound is effected may be acidic, neutral or alkaline depending upon the particular silver compound to be reduced and upon the particular metal which is to be dissolved therein to furnish the nascent hydrogen for the reduction. The reduction may be effected at any

suitable temperature. In many cases, it may be effected at about room temperature. A wide variety of metals may be employed for generating the nascent hydrogen in situ. It is only necessary that the metal selected be less noble than silver so that the aqueous medium in which the reduction is effected be incapable of dissolving silver but be capable of dissolving the added metal to generate the nascent hydrogen at the required rate. The reduction of the silver compound is conveniently effected in an aqueous alkaline medium in which a cheap and readily available metal such as zinc or aluminum is dissolved to generate the nascent hydrogen. These metals are preferably applied in a suitable finely divided form. During the reduction, the reaction mixture is preferably agitated, as by mechanical stirring or other suitable means, to insure even generation of the nascent hydrogen and efficient contact of the hydrogen and the material undergoing reduction. The reduction may, if desired, be effected in a closed vessel under superatmospheric pressure, preferably under a pressure of nascent hydrogen generated in the system or introduced into the system from an outside source.

After the reduction is complete, the precipitated silver is separated from the reaction mixture, washed free of salts and any of the added metal which did not react, and dried. To avoid loss of activity of the catalyst due to contact with the air, these operations are preferably conducted in a hydrogen atmosphere.

The catalysts prepared in accordance with the process of the invention may be used per se or in conjunction with one or more other metal or metal compound catalysts. They may, if desired, be supported on suitable catalyst carriers and supports such as charcoal, pumice, alumina, clay, etc. In some cases, the activity of the catalysts may be enhanced by incorporating therewith small amounts of promoter substances. Suitable substances for this purpose are platinum, gold, manganese, etc.

The silver metal and silver metal containing catalysts prepared in accordance with the process of this invention will be found highly advantageous and economical for use in a wide variety of chemical reactions, such as hydrogenations, oxidations, dehydrogenations, etc., conducted in either the liquid or the vapor phase because of their ease of preparation and their great activity at relatively low temperatures. Typical operations wherein the catalysts may be used to particular advantage are the hydrogenation of unsaturated hydrocarbons and unsaturated oxygen compounds, and the oxidation of saturated and unsaturated organic compounds.

In executing the process of the invention the olefine or olefines together with such diluents as may be present and the oxygen-containing gases are passed over the silver catalyst at a predetermined desirable rate and temperature. In general, the molecular ratio of olefine to oxygen passed to the catalyst is maintained greater than one to one although the ratio may vary widely depending upon the specific operating conditions. Excellent results are obtained when about 1.5 to 2.5 mols of olefine to one mol of oxygen are employed.

The temperatures which may be used in the process may vary considerably depending upon the olefine being oxidized, the rate of flow being used, the condition of the catalyst and other factors. The silver metal catalyst prepared in accordance with the invention permits the oxida-

tion to be conducted at temperatures as low as 125°C. or lower. It is ordinarily preferred to employ a temperature of from about 100°C. to about 500°C. It is usually desirable to employ as low a temperature as may be conducive to obtaining good conversions of the olefine to olefine oxide since undesirable side reactions are lessened at lower temperatures. The highest temperature beyond which it is not desirable to conduct the reaction is governed largely by the tendency of the particular olefine oxide produced to undergo further oxidation, rearrangement, and decomposition as well as the character of the olefine being oxidized, the activity of the catalyst, the rate of flow of the reactants and the pressure on the reaction system. In general, the temperature should be maintained at a point lower than temperatures at which pyrolytic side reactions are favored.

In general it is preferred to execute the process at atmospheric pressure or at slightly in excess thereof. However, if desired, substantially higher or lower pressures than atmospheric may be utilized.

The heat of the reactions which occur when the olefine is oxidized may be advantageously used to maintain the catalyst mass at the desired temperature. This may be done by suitably arranging the apparatus for such a purpose by methods well known to the art. For example, the reaction zone wherein the oxidation reactions occur may be fitted to heat the incoming reactants. By the use of such an arrangement a considerable economy of operation may be effected.

The exit products from the reactor may be passed to suitable condensing, absorption or adsorption equipment. Thus the olefine oxide and more non-volatile constituents may be separated from the unreacted olefine and other gaseous constituents. After removal of the olefine oxide, the unreacted olefine may be mixed with the desired amount of oxygen-containing gas and again introduced into the reaction zone.

The following examples illustrate suitable modes of executing the process of the invention. It is to be understood that the invention is not to be regarded as limited to the particular compounds, methods of operation and conditions shown in the examples.

Example I

Two silver plate electrodes were immersed in a 5% aqueous solution of potassium nitrate, and electrolysis effected by applying a current density of about 1 ampere/sq. decimeter. During the electrolysis, the liquid in the cell was kept in constant motion by vigorous mechanical stirring. As the electrolysis proceeded, the silver metal deposited on the cathode was washed and dried, while being kept out of contact with the air as much as possible.

The resulting silver metal catalyst was found to be particularly effective for catalyzing the oxidation of ethylene to ethylene oxide at relatively low temperatures. A mixture of two liters of ethylene and about six and a quarter liters of air was passed per hour over the heated catalyst contained in a pyrex glass reaction tube at a temperature of about 200°C. The effluent gas was found to contain ethylene oxide in an amount

corresponding to about 20% by weight of the ethylene treated. Thus, with the catalysts prepared in accordance with the invention, good conversions of ethylene to ethylene oxide can be obtained at lower temperatures than are required by the silver catalysts prepared by the known methods. The use of lower temperatures decreases the loss of applied ethylene caused by side reactions.

Example II

A silver nitrate solution having a concentration of about 0.04N was electrolyzed employing two silver metal plates, each of which had a surface of about 100 sq. cm., as electrodes and using a current intensity of about 1 ampere. Silver metal was deposited on the cathode in the form of a spongy, grey colored precipitate which was intermittently removed during the course of the electrolysis. The precipitated silver was washed with water to remove silver nitrate, subsequently washed with acetone, and then dried in a stream of nitrogen. During the separation, washing and drying of the catalyst, contact with the air was avoided as much as possible by working in a nitrogen atmosphere.

The powdered silver metal, prepared as above-described in the presence of nascent hydrogen was found to possess high catalytic activity for converting olefines to olefine oxides like the silver metal catalyst prepared in Example I.

Example III

To a solution of about 80 gm. of potassium hydroxide in 1500 c.c. of water was added drop by drop, while stirring vigorously, a solution of silver nitrate consisting of about 63 gm. of silver nitrate in 1000 c.c. of water. While the silver nitrate solution was being added, a total of about 6.6 gm. of aluminum metal grit was simultaneously introduced into the stirred mixture intermittently in small proportions.

The liquid was decanted from the resulting precipitate and the precipitate treated with about 1 liter of a 1 N potassium hydroxide solution for about half an hour at room temperature. The precipitate was then separated by filtration, washed with a 2 N potassium hydroxide solution until free of aluminum, washed with water until free of hydroxide, and subsequently washed with acetone.

A small quantity of the resulting catalyst product was freed of acetone by passing ethylene over it, and its activity as a catalyst for the oxidation of ethylene to ethylene oxide tested. A mixture consisting of ethylene and air in the volume ratio of 1 to 2 was passed over the heated silver catalyst. Oxidation of the ethylene to ethylene oxide was effected at temperatures as low as 125°C.

The present application is a continuation in part of my application Serial No. 218,635, filed July 11, 1938.

While I have described my invention in a detained manner and provide examples illustrating suitable modes of executing the same, it is to be understood that modifications may be made and that no limitations other than those imposed by the scope of the appended claims are intended.

GERARDUS HENDRICUS VISSER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR AROMATIZING AND DEHYDROGENATING HYDROCARBONS

Helmut Kolling and Walter Rottig, Duisburg-Hamborn, and Heinrich Tramm, Oberhausen-Holtten, Germany; vested in the Alien Property Custodian

No Drawing. Application filed August 22, 1939

In the known processes for producing aromatic hydrocarbons from hydrocarbons with a higher hydrogen content, it is necessary to make a fundamental distinction between removing hydrogen from saturated ring systems (naphthenes) and forming a ring from straight-chain hydrocarbons, more especially from paraffinic hydrocarbons. Naphthenic hydrocarbons admit of comparatively ready conversion into aromatic compounds by the use of simple catalysts. In the known increase in knocking of liquid fuels the problem should almost exclusively be one of converting saturated ring systems into aromatic ring systems.

For this purpose catalysts have already been proposed that consist of chromium precipitated upon a suitable carrier substance such as active carbon. It has already been proposed to employ, in the treatment of Pennsylvania benzines, mixed chromium catalysts that have been precipitated on magnesite.

Further, catalysts are known that are capable of forming aromatic substances from paraffinic hydrocarbons such as hexane or heptane, the catalysts being prepared with suitable carrier substances such as pumice stone, bleaching clays, Bentonite, magnesite, active carbon and the like and do not contain more than 10% of the active metal for example chromium. A particularly suitable proportion of chromium is given as being from 1 to 2%.

In addition to these chromium catalysts precipitated on carrier substances, contact substances are known for the same purpose that consist exclusively of chromium oxide.

It has been found that all these known aromatizing and dehydrogenating catalysts are suitable in the use of particular hydrocarbons only. It is not possible to produce—or at any rate only a very small quantity—aromatic hydrocarbons from a mixture of straight-chain paraffinic and olefinic hydrocarbons by their use. Such a conversion however has great practical importance, because for example in the synthesis of hydrocarbons from carbon monoxide and hydrogen, large quantities of such hydrocarbon mixtures are produced. In contradistinction to naturally recovered hydrocarbons, synthetic products contain practically no naphthenes.

For this reason it has not been possible to transfer either the experience secured in aromatizing natural hydrocarbons or the knowledge obtained in the dehydrogenation of pure aliphatic substances such as normal hexane or normal heptane, to the aromatizing of synthetic hydrocarbon mixtures. Experiments have shown that the

chromium catalysts heretofore described fail in the aromatization of synthetic hydrocarbons.

If for example a catalyst that has been produced for the dehydrogenation of normal hexane by the decomposition of chromium nitrate on pumice stone, be used, it is possible by its use to convert normal heptane to about 80%, into toluol at a temperature of from 460 to 480° C. When a heptane containing 10% of normal heptane be used the catalyst fails completely because polymers are formed that render the contact surface useless in a very short time.

When isomeric octanes that boil within a range of about 5° C are treated, the chromium catalyst also becomes inactive within a few minutes. Furthermore chromium catalysts precipitated on other carrier substances such as active carbon, are not suitable for the treatment of hydrocarbon mixtures.

It has now been found that a catalyst consisting of calcined magnesite as carrier and chromium oxide as activator is particularly suitable for aromatizing and dehydrogenating mixtures, under practical conditions, of aliphatic hydrocarbons of a wide boiling range when the content of chromium oxide is above 10% and advantageously between 30 and 50%.

Chromium oxide can be applied to the carrier substance in various known ways. Magnesite is advantageously impregnated a number of times with a solution of ammonium chromate, whereupon the ammonia is driven off by heat treatment, advantageously in the presence of reducing gases, so that chromium oxide is left behind.

An aqueous solution of chromic acid may be treated instead of solutions of ammonium chromate. In such case the catalyst is reduced with hydrogen or gases containing hydrogen at elevated temperature, for example at temperatures that are subsequently used for aromatization or dehydrogenation. Gases from which hydrogen breaks off such as hydrocarbon gases may be employed for reducing purposes.

Other solutions of chromium salts for example solutions of an organic character may be used for impregnating the magnesite; but solutions of chromium nitrate have not proved advantageous.

Besides chromium oxide, there may be added suitable promoters such as (compounds of Mn, Ni or Co and Th). In this way the catalytic activity of the chromium and magnesite contact substances used can be very considerably increased.

The following Example described a usable method of producing the catalyst employed.

Example 1.—1,000 gm of natural magnesite were calcined at 850°C. The carrier substance thus obtained was evacuated and thereupon impregnated with a solution of ammonium chromate saturated while cold. At the same time the magnesite was heated. After cooling the material was carefully dried, evacuated, and again impregnated with a solution of ammonium chromate. This treatment was repeated again and again until 1,000 gm of magnesite had absorbed about 400 gm of chromium oxide (Cr_2O_3). This mixture was dried at about 450°C. in a vacuum and allowed to cool in vacuum. Thereupon the conversion furnace was charged with the catalyst which was heated to the reaction temperature of about 480°C. within from 4 to 5 hours while a little hydrogen was passed through. The catalyst was then ready for use.

A conversion contact substance produced in this way has good dehydrogenating and aromatizing qualities.

At first this catalyst is particularly suitable for dehydrogenation, carried out without ring formation, of short chain paraffin hydrocarbons such as propane and butane as described in the following Example.

Example 2.—Propane was passed at a temperature of 480°C. over a catalyst consisting of 35% chromium oxide and 65% calcined magnesite at a velocity of 25 litres of gas per hour, per 1 litre of contact substance. The gas issuing from the reaction furnace contained about 15 to 20% propylene.

Such dehydrogenation of short chain paraffin hydrocarbons is generally carried out under atmospheric pressure. If the reaction be carried out under a partial vacuum, there is an increase in the yield of unsaturated hydrocarbons. The partial vacuum may be produced in the form of a reduced partial pressure by the admixture of inert gases (such as hydrogen or nitrogen) that do not take part in the reaction.

The catalyst produced, as described in Example 1, converts not only purely saturated aliphatic substances (such as normal hexane, normal heptane, normal octane or normal nonane) into aromatic substances with corresponding side chains such as benzene, toluol, xylol and the like; the catalyst is furthermore almost completely insensitive to the presence of olefines or isomeric aliphatic substances. Hence fractions of wide boiling range can be treated, for example all the benzines, boiling at between 60 and 150°C. derived from the hydrogenation of carbon monoxide.

The products obtained are light in colour like water and of a pleasant smell characteristic of the pure aromatic hydrocarbons.

Example 3.—Pure normal heptane was passed at a temperature of 460 to 480°C over a catalyst that consisted of 35% chromium oxide and 65% calcined magnesite. The product was toluol, that corresponded to an 80% conversion of the normal heptane used.

When aromatizing aliphatic hydrocarbons by the use of catalysts of chromium oxide and magnesite, there is produced a certain quantity of hydrocarbons in the form of normal gas in addition to the aromatic substances. Furthermore there are produced carbonaceous separations that render the surface of the catalyst inactive.

It has been found that these undesirable side reactions decrease or can be entirely avoided by mixing short chain aliphatic hydrocarbons with the aromatizing hydrocarbon mixtures. These aliphatic hydrocarbons may be either saturated

or unsaturated, and may consist for example of hydrocarbon gases with from 2 to 4 carbon atoms. The addition of olefinic hydrocarbons produces a higher yield of aromatic substances.

As the Examples that follow show, the formation of cracked gases can be lowered to such an extent that practically only additional hydrogen is produced. The ratio of the aromatic substances to the reaction gas produced corresponds, when normal heptane for example is treated, to the theoretic equation



The small excess of hydrogen is due to the formation of carbonaceous decomposition products.

Example 4.—Heptane was conducted at a velocity of 20 gm per hour at 480°C. over 300 cc of a catalyst of magnesite and chromium oxide, with about 25% by weight of chromium oxide. The final liquid product was a colourless mixture of heptane, heptene and toluol. The toluol content amounted to 44% by volume. From 100 gm. heptane there were obtained 82 gm. liquid products with 41 gm. toluol and 15 gm. gas or 3 gm. coke separations. The amount of gas produced was about 11% of the aromatic substances formed (ratio by weight).

Example 5.—Heptane was passed at a throughput velocity of 20 gm. per hour at 480° C. over 300 cc. of the catalyst referred to in Example 4. At the same time nitrogen moving at a velocity of 4000 cc. per hour was added. The resulting final product contained 40% by volume of toluol. From 100 gm. heptane there were produced 84 gm. liquid products, with 38 gm. toluol, also 13 gm gas and 3 gm carbonaceous products of decomposition. The gas produced amounted to about 30% of the aromatic substances formed (ratio by weight).

Example 6.—Heptane was passed at a throughput velocity of 20 gm per hour at 480° C. over 300 cc of the contact substance used in Example 4, and 4000 cc of propane were added per hour. The liquid products contained 42% by volume of toluol. From 100 gm heptane there were produced 91 gm liquid products. with 50 gm toluol. also 5 gm gas. and 4 gm decomposition products resembling coke. The gas produced amounted to about 10% of the aromatic substances formed (ratio by weight).

Example 7.—Heptane was passed at a throughput velocity of 20 gm. per hour over 300 cc. of the catalyst used in Example 4, and 4000 cc. of ethylene were also added per hour. The liquid products contained 63% by volume of toluol. From 100 gm. heptane there were obtained 90 gm. liquid products, with 62 gm. toluol. also 6 gm. gas and 4 gm. carbonaceous decomposition products. The gas produced amounted to about 10% of the aromatic substances obtained (ratio by weight).

Example 8.—20 gm. of a benzine fraction boiling between 96 and 160° C. were passed hourly over 300 cc of the catalyst used in Example 4, the benzine having first been separated from the products of the hydrogenation of carbon monoxide by the use of active carbon. The reaction temperature was maintained at about 460 to 480° C. The end products were 87% by weight of normally liquid hydrocarbons with 40% by volume of aromatic substances. There were at the same time produced 6.8% by weight of cracked gases and 3% by weight of coke separations.

The catalysts that were used according to the invention can be regenerated in a particularly easy way. To effect regeneration the hydrocar-

bon gases present in the contact substance are in the first place displaced by nitrogen. Thereupon air is passed over the catalyst at the conversion temperature employed, that is to say at about 480° C. After the displacement of the air by nitrogen the contact substance is treated for a further short period with hydrogen.

Such catalysts are effective for months with unvarying yield and at an unchanging conversion speed. It is an important fact that the catalysts differ from the conversion contact substances hitherto employed in that they contain a large quantity of chromium oxide, that is to say far above 10% and advantageously 30 to 50%.

Conversion can be effected both under ordinary pressure and under a slight superpressure or under a partial vacuum. The reaction is advantageously continued only until the hydrogen content of the final gas from which the liquid reaction products have been removed by condensation, amounts to at least 80%. Thereupon the catalyst is regenerated by combustion with air until the CO₂ content of the combustion gases has dropped to about from 1 to 5%. Thereupon the regenerated catalyst is further treated with hydrogen.

The catalysts according to the invention are very active not only in the treatment of the hydrocarbons obtained by the hydrogenation of carbon monoxide, but also for the conversion of the products of hydrogenation under high-pressure or in the conversion of natural hydrocarbon mixtures. If products of the hydrogenation of carbon monoxide are treated by means of the process hereinbefore described, it is advantageous to make use of the fractions that boil up to about 200° C, these fractions consisting wholly or for the major part of saturated hydrocarbons.

Conversion can be carried out in the usual apparatus employed for the purpose, which is used for example from 60 to 90 minutes for aromatizing and regeneration of the catalyst is then effected by calcination.

The objection arises that the catalysts prepared according to the invention incline to form powder. If the catalyst be employed in deep vertical layers the reaction is disturbed by this formation of powder. It has been found that these disadvantages do not arise if the catalysts referred to are used in less deep horizontal layers or slightly inclined layers. Advantageously reaction tubes disposed parallel are employed for the purpose, the tubes being heated within a common chamber with circulating flue gas. The temperature required for carrying out the conversion can be produced by heat derived from burners.

If carbon deposited on the catalyst be calcined, unalloyed iron tubes and the majority of alloyed iron tubes have imparted to them an injurious activity whereby the separation of carbon is facilitated. This objection thus leads to an increased formation of loose carbon on the walls of the tubes and affects the smooth course of the conversion. It has been found that these disadvantages do not occur if the conversion be carried out in reaction chambers that are made of a material that remains inactive even when air is blown through repeatedly. The most suitable reaction tubes are those made from a ceramic substance or metal tubes that consist of alloys having a considerable content of silicon or aluminium.

HELMUT KOLLING.
WALTER ROTTIG.
HEINRICH TRAMM.

ALIEN PROPERTY CUSTODIAN

MOULDING POWDERS

Stefan Bakonyi, Tovaros, Hungary; vested in the
Alien Property Custodian

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The invention relates to the manufacture of moulding powders, and is particularly concerned with the preparation of keratin-containing material in a form suitable for incorporation with a urea and/or thiourea formaldehyde condensation product, so as to produce moulding powders which yield moulded products having desirable properties of pale colour, clarity, resistance to water and to light, good machining properties, horn-like physical properties and freedom from moulding defects. The moulding powders flow well and are rapid-hardening. The process according to one feature of the invention is one in which keratin-containing material is refined to render it suitable for incorporation with a condensation product from urea and/or thiourea and formaldehyde into a moulding powder, by subjecting cleaned comminuted keratin-containing material to treatment firstly with an oxidising agent and then with a reducing agent.

The raw material may be hoofs, claws, horns, hairs, feathers and the like. The preferred material is hoofs, since these are purer, more elastic and less encrusted and give clearer and better keratin.

The raw material containing keratin is cleaned and ground to a granular meal. The meal is then digested with dilute acid, to which zinc chloride may be added, whereby iron, lime and other acid soluble impurities are removed. After washing with water the acid-free meal is treated by a mild oxidising agent which may be a 0.5-2% solution of slightly alkaline hydrogen peroxide. By the oxidation the material becomes paler, clearer and more plastic. After the treatment with the oxidising agent the material is washed with water and freed from reducible impurities by treatment with a mild reducing agent which may be a 0.5-1% solution of hydrosulphite or of another diluted reducing agent. The reducing treatment makes the material still paler, clearer, more plastic and more resistant against oxidation. The reduction treatment also removes the traces of the oxidising agent which, if not removed, would cause the material to darken during the hot moulding. After removing the reducing solution the material is washed with water and treated with a very dilute (0.1-1%) acid which may contain zinc chloride. Finally the material is dried at 45 to 65°C and ground to a fine flour which is a very clean keratin. Neither oxidising alone, nor reducing alone, nor firstly reducing and then oxidising produce a very clean keratin equivalent to the product of the process

described above. It is necessary firstly to oxidise and then to reduce, as above described.

The refined keratin flour is mixed with condensation products from urea and/or thiourea and formaldehyde, if necessary or desired with addition of condensation product from phenol and/or cresol and formaldehyde and of other synthetic resins, dried and ground. According to one feature of the invention a condensation product containing excess formaldehyde is first made and, in a later stage of the preparation, an amount of urea and/or thiourea sufficient for this excess is added. Furthermore, an acid catalyst is added, which acts as a condensation agent for the excess formaldehyde and as an accelerator for the curing of the moulding powder. The acid catalyst may be added to the dried product before grinding. As acid catalysts the preferred compounds are high molecular polybasic organic acid anhydrides, acids or acid esters which are sparingly soluble in the condensation mixture and act as condensing agents only at the high temperature used for pressing when they dissolve in the molten mass and bring about rapid hardening. Examples are phthalic anhydride, adipic, sebacic and succinic, phthalic and resinic acids, or their acid esters. An organic amine may be added to the condensation mixture to improve the wetting properties. As an accelerator of the condensation and as a buffering agent ammonia may be added to the condensation mixture. The condensation mixture is mixed with the refined keratin flour, dried and finely ground. By hot moulding this powder melts to a homogeneous mass and gives nearly clear mouldings.

For improvement of the water resistance and chemical resistance the condensation mixture may as stated above be mixed with phenol and/or cresol and formaldehyde condensation products or with other synthetic resins containing formaldehyde. The phenol and other resins also form with the other components homogeneous products since the urea resin acts as a mutual solvent for the keratin and the phenolic resin. It is not possible to form a homogeneous mass from phenolic resin and keratin without urea resin.

The mouldings made according to the invention are pale, water and light resistant and easily moulded, but they are not so brittle as the majority of commercial aminoplastics; they can be easily be turned, drilled and tapped and worked by all methods as casein plastics, natural horn, ivory and cast resins. Whilst the majority of commercial aminoplastics are brittle and accord-

ingly are generally used in connection with cellulose fillers which have the disadvantage of rendering them opaque, the mouldings according to the present invention are almost clear.

The invention is illustrated by the following examples.

Example 1

I. 200 kg of cleaned hoofs are broken down into pieces of 5–20 mm diameter, dried at 45–65°C and ground to a granular meal. Soft hoofs, such as those from calves, sheep or swine may be planed into chips. The meal or the chips are treated with 800 litres of 1–2% iron-free HCl at 30–36°C for 12–24 hours with occasional or continuous stirring 0.4–0.6 kg ZnCl₂ may be added to the acid solution. After the treatment the material is freed from the acid solution in a centrifuge and washed with water until the wet meal shows a pH=6. Next the material is placed in a 1% weakly alkaline solution of hydrogen peroxide and again allowed to stand for 12–48 hours or longer at 30–36°C with stirring. The reaction of the bath is maintained weakly alkaline throughout. For greater economy the hydrogen peroxide may be added to the bath in several portions. At the end of the treatment the liquor is separated from the solid in a centrifuge and the latter is washed with water until no reaction is observed with starch iodide paper. The material is then treated with 800 litres of 0.8–1% Na₂S₂O₄ solution and stirred occasionally for 12–24 hours at 30–36°C. The material is separated from the bath and washed with a 0.1–1% solution of acid i. e. formic acid and finally washed with water until the wet meal shows a pH=6. It is then dried at 45–65°C and ground to a fine flour (2500 meshes to a square cm.). The yield is about 180 kg. The separated liquors are filtered, brought up to strength and used again, so long as they do not become too dirty.

II. 100 kg urea (or a mixture of 85.7 kg urea and 18.1 kg thiourea) are dissolved in such a portion of commercial formalin (40% per volume or 30% by weight) as contains 100 kg of gaseous formaldehyde and neutralised with 3–4 litres of 25% ammonia solution. Now 0.25 kg ethylene diamine are added and the reaction mixture is allowed to stand for 18–24 hours at about 20°C. At higher temperatures this time becomes shortened.

III. The condensation mixture prepared as in II. may be mixed with 14.3 kg urea (or 18.1 kg thiourea) so that the molecular proportion of urea (thiourea) to formaldehyde is brought to 1:1.75. Then 0.45 to 0.85 kg of phthalic anhydride or an equivalent amount of phthalic monoglyceride or the equivalent quantity of adipic acid or of adipic monoglyceride is added in alcoholic solution. After mixing well the reaction mixture becomes a syrup.

IV. The condensation mixture made according to II. or to II. and III. is mixed with the refined keratin flour prepared as in I. and kneaded well for 1 to 2 hours in a stainless mixing machine. The cream-like mass is extruded in thin rods from a stainless extruding machine, and these rods are then dried either in a stream of air or

in vacuum at about 50°C for 4 to 8 hours. The dry product is then finely ground.

The moulding powder manufactured in this way is moulded at 140–145°C under a pressure of 180–500 kg per sq. cm. with a curing time of ¼ to ¾ minute per mm thickness. Very pale, nearly clear, brilliant, water and light resistant and mechanically strong mouldings are made, which can be worked by turning, drilling etc. The material can be coloured by known methods and made to produce mottled effects similar to buffalo horn, tortoise-shell and the like. The material flows so well that not only buttons, but also large and complicated mouldings can easily be made, for example boxes, frames, vases, cameras, radio cases, lamp shades, household fittings, typewriters, automobile accessories, fancy goods and the like. The mouldings can afterwards be worked by mechanical processes and this is in many cases necessary. If the operation III. of example 1 is omitted, the excess formaldehyde is partially lost but the clarity of the mouldings is increased.

Example 2

Working according to example 1 the condensation mixture under II. or under II. and III. is mixed with 33 kg of phenol and/or cresol formaldehyde condensation products and 2.7 kg hexamethylenetetramine. The amount of the refined keratin flour is increased to 200 kg. The moulding powder made in this way is still more resistant to water but less resistant to light and gives mouldings suitable for chemical and electrical industries.

Example 3

Working according to example 1, the amount of refined keratin flour is increased to 495 kg and sufficient water added to make the dough easy to mix. There results a moulding powder which is similar to that made in accordance with example 1, but which flows less under the press and is less resistant to water. This moulding powder is suitable for cheap articles, since the cheapness of the keratin raw material makes the manufacture cheaper than that of other moulding powders containing great quantities of artificial resins.

The proportion of keratin flour to urea resin or phenol (cresol) resin can also be different from the above proportions, e. g. from about 3:1 to about 1:3. Raising the keratin content, lowers the water resistance and the flow. Lowering the keratin content under 1:1 slightly reduces the ease of machining. The sensitivity to water of mouldings rich in keratin can be reduced by immersion in formalin.

Example 4

Working as in example 1, the hoofs are replaced by horns. The flow of the moulding powder and the clarity of the mouldings is lower but the mechanical strength is very good. By using feathers instead of hoofs, very good flow and clarity is obtained. Analogous results are obtained with hairs.

STEFAN BAKONYI.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREPARATION OF POLISHING WAX

August Schneider, Hamburg, Germany; vested in
the Alien Property Custodian

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This invention deals with an improvement in floor waxes, and more particularly relates to a water-free floor wax composition giving a glossy covering which is not slippery.

Floor wax compositions which are free from water normally consist essentially of paraffin and natural waxes, ozokerite, and a suitable solvent. Suitable waxes are in particular ceresin or mixtures thereof with natural waxes such as beeswax, which mixtures contain a predominating amount of paraffin wax. Ozokerites or similar substances are used in mixtures of this type because they inhibit the crystallization of the wax, thereby making the mixtures smooth. The usefulness of ozokerites in floor waxes is, as a matter of fact, judged by their ability effectively to inhibit crystallization.

Frequently, in addition to the above components, small amounts of resins are added to improve the homogeneity of the resulting mixture. However, floor waxes containing substantial amounts of resins yield floor coverings of considerable stickiness. Moreover, the melting point of the mixture is usually considerably depressed so that it may be necessary to add additional amounts of high melting ceresins, thereby increasing the tendency to form a granular product.

It has now been found that floor waxes of a high degree of smoothness can be produced if the ozokerite is substituted by a highly viscous mineral oil to which has been added a small amount of an oil-soluble resin. Suitable resins are, for example, the formaldehyde-phenol condensation products. About 3% to 15% of the resin may be added to the mineral oil, and a preferred ratio of resin to mineral oil is about 5:95.

Any mineral oil having a viscosity above 2° Engler at 100°C is suitable, whether it be a raffinate, extract, distillate, etc., provided it is substantially free from tarry material. In floor waxes containing the mineral oil-resin solution, the role of this solution is primarily that of ho-

mogenizing and reducing the tendency of the wax to crystallize. When brushed on the floor, the surface of the wax is glossy and smooth. The small amounts of resins prevent its being slippery, and it has the advantage over similar mixtures containing ozokerite of not being sticky.

Because of the peculiar structure of mineral oils, the floor wax produced according to my invention produces a very tough coating which is superior in all respects to similar coatings containing ozokerite.

The ratio between paraffin wax, e. g., ceresin, and the resin-in-oil solution may vary within fairly wide limits, which to some extent depend upon the melting point of the paraffin as well as its tendency to crystallize. In general, about 2% to 10% of the resin-in-oil solution is added to the paraffin, and the resulting mixture may be combined with a suitable solvent, such as kerosene, to reduce it to a consistency suitable for applying it with a brush.

Example

The following components were melted in a conventional grease kettle: 300 kg. of mixed waxes consisting of 250 kg. paraffin (melting point 52°C) plus 50 kg. beeswax. Into the melted wax, 10 kg. of a solution of 5 parts of phenol-formaldehyde condensation product in 95 parts mineral oil having a viscosity of 4° Engler at 100°C, were added. After thoroughly mixing the components, about 700 to 1000 kg. of a conventional solvent was incorporated.

The resulting product was a smooth floor wax having excellent qualities. When applied to the floor with a brush, it gave a glossy covering which was smooth, but was neither slippery nor sticky. It was hard enough not to give imprints when stepped upon. It remained satisfactory even on the hottest summer day. Moreover, it was very economical when applied to the floor surface with a brush.

AUGUST SCHNEIDER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF GLYCERINE

Giulio Natta and Rolando Rigamonti, Milan, Italy; vested in the Alien Property Custodian

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It is already well known that glucose and other carbohydrates may be reduced by means of hydrogen under pressure with formation of different products as propylenglycol, methyl alcohol, ethyl alcohol and also according to some authors, with formation of small quantities of glycerine.

According to Zartmann and Adkins (J. Am. Chem. Soc. 55, 4559, 1933) there are obtained methanol, alcohol, water, propilenglycol and high boiling fractions containing 1-oxyethyl-3-oxy-1,3-dioxolane polyvalent glycols as the tetraoxyhexan and the trioxyhexan and according to the "I. G. Farbenindustrie A. G." also propan and propylalcohol (Italian Patent 291,568 of 23rd 8, 1930).

The quantity of glycerine to be obtained with the processes of hydrogenation till now known is always small and not such as to allow an industrial starting of the same processes for the production of glycerine.

On the other side the processes of fermentation show relatively how yields about the 30-35% of the glucose employed and cannot be increased practically since part of the glucose is destroyed in the formation of alcohol, carbonic anhydride, acetaldehyde and other secondary products.

The present invention allows on the contrary to obtain high yields of glycerine, much higher than that obtained through fermentation causing the hydrogenation of the glucose and other sugars and carbohydrates to take place in particular conditions and by means of particular catalysts without the formation of products of an high hydrogenation, as propylalcohol, ethyl alcohol, hydrocarbons and the like.

It was on the contrary possible by varying the conditions in which the hydrogenation is conducted to obtain different proportions between glycerine and propylenglycol, for instance to obtain more glycerine and less propylenglycol or to obtain nearly no glycerine and exclusively the product of subsequent hydrogenation that is the propylenglycol with practical quantitative yields without the formation of secondary products.

It results then possible to conduct the hydrogenation in such a way as to obtain prevalently one than another of the products wanted.

Such really important results have been obtained by causing the hydrogenation to take place at a temperature exactly determined and by subjecting the products to a determined working cycle.

The process according to the present invention consists in hydrogenising the glucose and other

carbohydrates to be easily transformed in glucose through hydrolise (cane sugar, starch, cellulose destrin and the like) or of hydrogenation products thereof (sorbite, mannite and the like) at temperature higher than 200°C, and preferably below 270°C in the presence of convenient catalysts. The product of hydrogenation is distilled in order to separate propylene-glycol and glycerine formed, the residual being hydrogenised again. By this way the nearly totality of the starting product may be hydrogenised without any loss owing to secondary reactions.

The operation of hydrogenation has to be conducted in presence of solvents as water, methyl alcohol, ethyl alcohol or superior alcohols, preferably methyl alcohol or ethylalcohol.

The catalysts may be of different nature for instance with a basis of chromite of copper prepared by means of thermic decomposition at a low temperature, of double chromate of copper and ammonium or with a basis of copper and nickel.

Active catalysts of this last type may be obtained by reduction of solid solutions obtained by means of coprecipitation of hydroxides or basic carbonates, or oxalates or other organic salts of copper and nickel or of copper and cobalt. The solid solutions among the salts or isomorphous hydroxides may be introduced into the chamber of reaction even without a previous reduction.

According to the temperature and the duration of heating it is possible according to the invention to vary the quantity mentioned of propylenglycol and glycerine obtained, in the sense to increase the proportion of the former with respect to the latter by increasing the temperature and the duration of hydrogenation.

A high yield of glycerine for instance may be obtained by using a very active catalyst for instance one containing copper obtained by means of the Natta-Roberti process (Italian patent application n. 7330/38 of 6th August 1938) and causing the hydrogenation to take place at a temperature lower than 250° C and preferably about 220-240°C but always by effecting short durations of hydrogenation. These depend also on the quantity of the catalyst used.

The hydrogenation may be executed in a discontinuous way or preferably continuously.

In the first case the reaction is stopped after 1-5 hours of reaction according to the activity of the catalyst and the pressure, through cooling or discharging of the hydrogenised product from the apparatus of reaction. The catalyst eventually transported is separated for instance

by filtration or centrifugation, the glycol and glycerine are distilled and the residue is put again into the cycle eventually added to small quantities of fresh catalyser.

In the second case the alimentation may take place without interruption in a column resistant to a high pressure and heated from the outside at a constant temperature (for instance with condensing vapours). The discharge may also be continuous or intermittent, as also the introduction of hydrogen for replacing the quantity consumed may be equally continuous or intermittent.

In the case of a continuous functioning the catalyser may be a fixed one and constituted by solid solutions of nickel and copper precipitated on a siliceous or aluminous support and the contact between these solutions and the liquid is secured by the circulation of the liquid which is made to fall on the catalyser.

This system possesses advantages over the methods of agitation with an agitator inside the chamber of reaction and over those based on the shaking of the whole apparatus.

It is necessary in order to obtain a considerable yield of glycerine to extract the liquid before the hydrogenation is too much advanced. It is convenient to stop the hydrogenation before the quantity of glycerine decomposed by further hydrogenation surpasses the half of the quantity of glucose hydrogenated to glycerine or still further. It is possible to realize this more easily if the hydrogenation is executed in such a way that the product may be subjected to a fractioned distillation and rectification at a low pressure in order to separate the glycerine formed and the residue of the distillation may be introduced again into the cycle to be further hydrogenated under pressure. For instance by subjecting a solution of glucose in alcohol in the proportion 1:2 with the addition of the 2% of the catalyser, comprising chromite of copper obtained with the Natta-Roberti method above cited to a hydrogenation at 230°C with a duration of 3 hours in continuous stirring there were obtained 130 parts of glycerine for each 100 parts of propilenglycol formed at the same time, while the residue of hydrogenation resulted for the greater part constituted by sorbite which may be introduced again into the cycle and transformed into glycerine.

At higher temperatures of about 240°-250°C more propylenglycol is obtained. For instance with saccharose for subsequent hydrogenations, each time with separation of the products formed, a transformation of about 50° of saccharose into glycerine and of about 50% into glycol was ob-

tained through the recuperation of the residues. It should on the contrary be executed a complete hydrogenation in an only operation of 5 hours at 270°C there is obtained the 71% of glycol and barely the 6% of glycerine. The residue may be still hydrogenated into glycol and glycerine.

By reducing the duration of the hydrogenation greater total yields in glycerine and smaller in glycol may be obtained, but there will ensue greater expenses for the separation of the solvent and the residues which are present in a larger proportion.

The separation of the glycerine may be effected as already mentioned by distillation or better rectification at a low pressure: separating first all the most volatile solvent, then the propylenglycol and at last the glycerine. The residue of the hydrogenation may be subjected again to hydrogenation alone or mixed with carbohydrates to be hydrogenated.

The process may be continuous with great advantage for the thermic and economical yield by introducing the products to be hydrogenated continuously in a column or in a series of pressure resisting tubes, fed at one end (for instance from above), while at the other end (for instance from the bottom) there discharged also continuously the products of the hydrogenation, which may be subjected afterwards to a rectification also continuous.

The residue of the rectification in such a case may be introduced also continuously into the hydrogenation apparatuses.

The catalyser may be mixed in powdery form and kept in suspension in the liquid to be hydrogenated or and preferably in the case a diluted solution or a very pure product is employed, fixed catalysers may be used with the advantage of simplifying the process by avoiding the separation of the catalyser in suspension from the product of hydrogenation. In this case the fixed catalysers, contained inside the hydrogenating apparatus, are dipped into the solution to be hydrogenated eventually preheated.

It is also possible to hydrogenate not soluble carbohydrates for instance polyosis, cellulose starch, wood and the like.

In this case the catalyser has to be transported and kept in suspension together with the carbohydrate in an aqueous or hydroalcoholic liquid, kept in agitation. This case is similar to the pre-calling ones when the hydrolise of the polyosis precedes the hydrogenation, but there is the advantage of reducing the number of the operations.

GIULIO NATTA.
ROLANDO RIGAMONTI

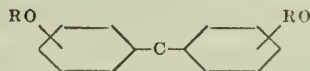
ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCTS FROM SUBSTANCES OF THE TYPE OF DIHYDROXY-DIPHENYLMETHANE AND PROCESS OF MAKING THEM

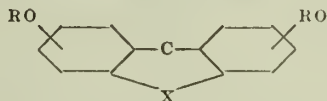
Erich Haack, Radebeul, near Dresden, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed October 3, 1939

The object of my invention is the production of new condensation products from substances containing the dihydroxy-diphenylmethane-group arrangement, and methylolamides of aliphatic, aromatic or mixed aliphatic-aromatic carboxylic acids. These condensation products have a special value as remedies, especially as purgatives, and also as intermediates for the manufacture of remedies. My invention also refers especially to the production of the new substances by the interaction of methylolamides of the organic acids mentioned and compounds containing a dihydroxy-diphenylmethane group of the following kind:



wherein R means hydrogen, alkyl- or acyl-groups. The benzene nuclei may be substituted, e. g. by alkyl groups. The groups may also be linked to each other, a group arrangement of the following kind thus resulting:



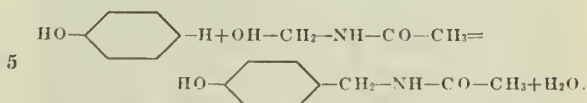
Herein X represents the methylene or carbonyl group. Suitable compounds of both of the types mentioned are e. g. 4,4'-dihydroxy-diphenylmethane and its derivatives when substituted by alkyl or aryl in the methane-group or by alkyl in the benzene nucleus. 4,4'-dihydroxybenzophenones or their alkyl-derivatives respectively alkyl ethers, may also be used in the same way. Further starting materials are for instance the following:

Phenolphthaleine and Cresolphthaleine, diphenol- and dicresolindolinon, hydroxyanthraquinones and others. As acidamides may be used for instance the amides of the acetic, propionic, butyric, valeric, isovaleric, caproic, caprylic, capric acids and their higher homologues, furthermore of the lactic, phenylacetic, mandelic, benzoic, salicylic and similar acids, also of the carbonic acid in the form of ureas and urethanes.

The foregoing statements are naturally meant to specify only a few of the condensations possible according to my invention.

The reaction between methylolamides of carboxylic acids and phenols or their derivatives is known and takes place e. g. when reacting with

methylolacetamide on phenol according to the following equation:



Here, the acylated methylolamine-group may enter into p- or o-position to the phenolic hydroxyl, or two groups may enter into o- and p-position, also in o- and o'-position if the p-position is already taken. But generally only one methylolamide-group enters into reaction with one phenolic hydroxyl, especially if the p-position is taken. The simple compounds of this kind known heretofore are of no technical interest worth mentioning and have no value, especially not as purgatives, while the condensation products as produced according to my invention from compounds containing a dihydroxy-diphenylmethane-group and based on the same reaction scheme, are valuable remedies and purgatives.

As I have found, the condensation of the compounds containing a dihydroxydiphenylmethane group arrangement with the methylolamides of organic carboxylic acids takes place especially well in the presence of condensing agents, e. g. acids like hydrochloric and sulphuric acid, salts like chloride of zinc and other dehydrating agents like phosphorous chloride or oxychloride. According to the general reaction scheme illustrated above, as a rule one or two methylolamide groups enter into the dihydroxydiphenylmethane.

The new condensation products possess a very strong and reliable action as purgatives already per se. However, I have found furthermore, that this action may be increased considerably, if these compounds are brought into a form which when dissolved makes the active substance free in a very fine state of division. This is obtained by imbedding the substance in the finest state of suspension or colloidal division into a soluble colloidal carrier which is able of swelling and digestible and, when dissolved, leaves the substance in such a fine state of division, that it is soluble in the contents of the intestines. The compounds for instance, according to my invention, are dissolved in an alkaline medium, like sodium hydroxyde solution, or in an organic solvent, like alcohol, and then precipitated by adding water or acids in the presence of a protecting colloid like gelatine, crystal gum, albuminous substances, decomposition products of starch and such like. Thereby, the active compound sep-

arates out in a very fine division so as to allow the formation of a white milk. The latter may be dried carefully or absorbed in other substances. The active substance may also be caused to flocculate from its solutions together with albuminous substances like casein. According to the present invention, the active purgatives may also be put into the finest state of division by the most varying methods known and be applied together with substances innocuous to the human body.

My invention is illustrated by the following examples without being restricted thereto.

Example 1

	Grams
Diphenolisatin -----	40
Chloride of zinc-----	60
Glacial acetic acid-----	120

are dissolved hot and, after cooling down, mixed with 52 g methylolamide of isovaleric acid (=3 mol) which dissolves readily. After standing for 24 hours at room temperature, the solution is run in a thin jet into a mixture of 2000 cc of water and 100 cc of concentrated hydrochlorid acid. The granular mass is sucked off, washed well with water and hereafter dissolved in 1000 cc of a 2% sodium hydroxide solution and twice shaken out with ether for removing neutral constituents. After filtering off an insoluble residue, the solution is run with stirring into a mixture of 1000 cc of water and 50 cc of concentrated hydrochloric acid and, after standing for some time, sucked off and washed with water. The yield, when dry, is 70 g as calculated for 1 mol Diphenolisatin+2 mol methylolamide of isovaleric acid-2 mol water. The compound dissolves readily in 1% sodium hydroxide solution. The solutions are able to foam and, with potassium ferricyanide, give a violet-red colouring.

Example 2

When using only 1 mol of methylolamide of isovaleric acid, a condensation product is obtained which is similar to that one contained in example 1 but dissolves more readily. The colour reaction with potassium ferricyanide is dark red.

Example 3

When using 65 g of methylolamide of caprylic acid in example 1 instead of the 52 g of methylolamide of isovaleric acid, 91 g of a condensation product is obtained which shows a blue colouring with potassium ferricyanide in sodium hydroxide solution. This compound contains two caprylic acid amide groups.

Example 4

If according to example 3 the condensation is carried out with 22 instead of 65 g methylolamide of caprylic acid, a monocaprylic derivative results. By dissolving the crude product in methylalcohol and precipitating with 2.5% sodium carbonate solution, it can be separated from diphenolisatin which may occur in the raw product but readily dissolves in 2.5% sodium carbonate solution. About 52 g of a white powder are thus obtained which is easily soluble in 1% sodium hydroxide solution to give foaming solutions; it turns violet upon adding potassium ferricyanide solution.

Example 5

	Grams
Diphenolisatin -----	30
Chloride of zinc-----	60
5 Glacial acetic acid-----	120

are dissolved hot and after cooling down mixed with 37 g methylol- α,α -dimethylurea. After heating it to 50° C for 4 hours, the mass is run into 1500 cc of water +50 cc of concentrated hydrochloric acid which being agitated. The precipitate being sucked off and washed, is dissolved in 1000 cc of 2% sodium hydroxide solution and then precipitated with 2000 cc of water +50 cc of concentrated hydrochlorid acid. When dry, 47.5 g of a white powder are obtained, 49 g being calculated for 1 mol diphenolisatin+2 mol methylol- α,α -dimethylurea - 2 mol water. The product is difficultly soluble in ether and benzene, but easily dissolves in alcohol and is not precipitated from the alcoholic solution by the addition of 2.5 % sodium carbonate solution. The compound gives a violet-red colouring with potassium ferricyanide.

Example 6

If a solution of 20 g Phenolphthaleine and 60 g chloride of zinc in 120 g glacial acetic acid is condensed with 27 g methylolamide of caprylic acid at 50°C., a crude product is obtained which after being dissolved in alcohol and precipitated by 2.5% sodium carbonate solution, is dissolved again in caustic soda lye and, after being separated from the insoluble portion, precipitated as a white powder by diluted hydrochlorid acid. The substance dissolves in diluted caustic soda lye with dark violet colour, the solutions foaming strongly.

If the condensation products as described in the examples are to be brought into a finely divided state especially active and suitable for medicinal use, they are dissolved e.g. in an alcoholic solution containing alkali, mixed with gelatine and crystal gum and then precipitated by a watery solution of hydrochloric acid, citric acid or other suitable acids, or the precipitations as described in the foregoing examples are carried out in the presence of protecting colloids. The resulting milky product is brought to dryness in a suitable way, e.g. by treating it with a dry stream of air. Instead of alcohol and caustic soda lye, other solvents may be used, instead of gelatine, other protecting colloids. By using flocculating colloids like casein, the products may also be precipitated in a very fine state of division.

Condensations, corresponding to the examples mentioned above, with methylol-benzamide and methylolamide of salicylic acid take place in the same way as described in the examples. The present invention also includes other variations, e.g. the use of solvents and condensing agents other than acetic acid + chloride of zinc, like concentrated sulphuric acid. In a similar way, the hydroxy- or alkoxy-diphenylmethane derivatives mentioned in the description, may also be condensed with methylolamides of acids.

ERICH HAACK.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF COLOURS FOR PRINTING, PRODUCTS RESULTING THEREFROM AND THEIR INDUSTRIAL APPLICATIONS

André Henri Victor Durr, Paris, and René Wendling, Creil, France; vested in the Alien Property Custodian

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It is known that paints may be prepared by grinding emulsions of siccative glycerophthalic resins in water with pigments, but the colours thus obtained when they are used in the printing of textiles have the disadvantage of giving decorative effects of poor fastness to washing and rubbing.

The present invention relates to a process which allows new colours to be obtained for printing, not having these disadvantages; this process is characterised by the fact that a siccative glycerophthalic resin is ground with a pigment, if desired in the presence of solvents for the resin and that the pigmented enamel thus obtained is emulsified in water. While, according to the above described known process, the pigment was ground with the emulsion, according to the present invention the grinding of the pigment is effected firstly with a solution of the siccative glycerophthalic resin and the preparation of the emulsion is effected subsequently; the pigment is thus perfectly surrounded by the resin thus giving decorative effects which are very fast to washing and rubbing.

The siccative glycerophthalic resins employed for carrying out the invention may be prepared according to any known process, they should contain at least the radicles of phthalic acid, glycerine and siccative fatty acid, but may likewise contain radicles of other polybasic acids, other polyalcohols, monoalcohols or monobasic acids other than the siccative fatty acids.

For example, it is possible to use mixed glyceromaleophthalic resins or glyco-glycerophthalic resins containing residues of soya fatty acids. The fatty acids or their mono, di, or triglycerides which may be used for the manufacture of these resins are in principle all those which in the paint, lacquer and varnish industries are known to act as dryers but preferably those will be employed which do not become yellow under the influence of air and light, such as the derivatives of soya oil or dehydrated castor oil.

The resins may be used alone or with one or several dryers, by which are meant the metallic dryers which are used in the varnish industry, as examples of which may be mentioned cobalt, lead and mangan dryers.

The pigments used may be of organic or inorganic nature. The solvent in the presence of which their grinding with the resin may be effected may be constituted by a single body or a mixture and will preferably be chosen from the light or medium solvents. It may be useful to add to the solvent a plasticiser or a small quan-

tity of heavy solvent so as to improve the properties of the resin or the conditions of evaporation of the solvent.

The emulsion in water of the pigmented enamel obtained as has been explained above, may be effected with one of the emulsifiers whose employment is known in the industry; as examples of such emulsifiers may be mentioned water-soluble cellulose derivatives, such as methyl cellulose, ethyl cellulose and hydroxyethyl cellulose, polyvinyl alcohol, partially saponified and water-soluble polyvinyl acetates, water soluble reaction products of ethylene oxide with organic substances insoluble in water and containing a reactive hydrogen atom, casein, salts of carboxylic and sulphonic acid or sulphuric esters of high molecular weight. To facilitate emulsion auxiliary products may be added such as water soluble solvents, ammonia, volatile amines, triethanolamine.

The above described printing colours may be also obtained in form of concentrated pastes containing the resin, the pigments and the suitable emulsifying agent in water. These pastes may be warehoused in concentrated form, and transformed just before use in printing colours of the desired viscosity, by addition of suitable solvents for the emulsion, comprising an organic solvent on one hand and water on the other hand. It is understood that the addition of those suitable solvents to the emulsion renders possible the obtaining of printing pastes of any suitable viscosity. The viscosity can be thus adjusted on a very wide scale.

The colours thus obtained may be printed readily, have a viscosity which may be regulated according to the desires of the printer by suitable choice of the resin, solvent and emulsifier and of the proportions thereof. The printed fabrics are then dried at temperatures which may vary from ordinary temperature to 200° C. the drying being more rapidly effected the higher the temperature.

The decorative effects obtained are very fast to washing and rubbing and the printing cylinders may be easily cleaned after working by washing with hot water.

The following examples illustrate the invention:

Example 1

100 parts of siccative glycerophthalic resin with a basis of dehydrated castor oil are ground, after addition of xylene and driers if desired with 20 parts of the dye known in commerce under the

name "Lutetia Scarlet NRSF" so as to obtain a pigmented enamel of the constitution:

	Parts
Resin -----	100
Lutetia Scarlet NRSF -----	20
Xylene -----	200

On the other hand, 10 parts of methyl cellulose are dissolved in 390 parts of water containing one part of triethanolamine and then the pigmented enamel mentioned above is added in portions. There is thus obtained a printing-colour which may be printed easily and which, after drying for five minutes at 110°C. or at a higher temperature, has a good resistance to rubbing and to washing. The printing cylinders may easily be cleaned after working by washing with hot water.

Example 2

90 parts of siccative glycerophthalic resin with a basis of dehydrated castor oil are ground after addition of xylene and a dryer if desired, with 10 parts of the dye known in commerce under the name of "Fast Monastral Blue BS" in a cylinder grinder so as to obtain a pigmented enamel of the constitution:

	Parts
Resin -----	90
Fast Monastral Blue BS -----	10
Xylene -----	60

On the other hand, 10 parts of methyl cellulose are dissolved in 390 parts of water containing one part of triethanolamine and then in portions is added a solution of 10 parts of ethylcellulose in 140 parts of xylene, and the pigmented enamel is prepared in the conditions mentioned above. Thus there is obtained a printing colour which may be printed easily and which after drying for five minutes at a 110°C. or if desired at a higher temperature, shows a good resistance to rubbing and to washing. The printing cylinders may easily be cleaned after working by washing with hot water.

Example 3

60 parts of a glycerophthalic resin with a basis of dehydrated castor oil are ground, after addition of xylene and a dryer if desired with 10 parts of the dye known in commerce under the name "Fast Monastral Blue GS" in a cylinder

grinder so as to obtain a pigmented enamel having the constitution:

	Parts
Resin -----	60
Fast Monastral Blue GS -----	10
Xylene -----	60

On the other hand, 10 parts of methyl cellulose are dissolved in 390 parts of water containing 5 parts of triethanolamine and there is added in portions a solution of 40 parts of glycerophthalic resin which dries in the furnace with a basis of soya oil and the pigmented enamel prepared as described above. Thus there is obtained a colour which may be printed easily and which after drying for five minutes at 110°C. or a higher temperature has a good resistance to rubbing and washing. The cylinders may readily be cleaned after working by washing with hot water.

Example 4

A. 300 parts of a siccative glycerophthalic resin with a base of dehydrated castor oil, and having a composition corresponding to 45% of glyptal and 55% of drying oil are diluted with 75 parts of xylene. The mass thus obtained is ground with 45 parts of the dye known in commerce under the name "Heliotrope brilliant Lamprolac NRL extra poudre" upon a roller mill until complete homogenisation has occurred (this being controlled upon a glassplate).

B. On the other hand, 45 parts of methycellulose are dissolved in 405 parts of water, and 15 parts of triethanolamine are added.

The two parts A and B are coarsely mixed and passed through a finishing grinder. The paste thus obtained contains 44,8% of dry residue.

For the use this paste is diluted first with 60% of its weight with xylene (containing if desired a cobalt dryer in the proportion of a volume of 2% cobalt dryer for 100 parts of the final printing colour), and then with 85% in weight of water under stirring.

The printing colour finally obtained and ready for use contains 18,3% dry residue. This printing colour may be easily printed and shows after drying for a few minutes at 110° C. or if desired at a higher temperature a good resistance to rubbing and to washing. The printing cylinder may be easily cleaned with hot water.

ANDRÉ HENRI VICTOR DURR.
RENÉ WENDLING.

ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCTS OF SUPER-POLYAMIDE CHARACTER AND PROCESS OF PRODUCING THEM

Hanns Ufer, Hans Schoenherr and August Weickmann, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 9, 1939

The present invention relates to condensation products of superpolyamide character and to a process of producing same.

In the co-pending application Ser. No. 252,630 one of the present inventors and two others have described a process for the production of high molecular compounds of the polyamide type according to which amines having at least two reactive amino groups separated from each other by at least two carbon atoms are reacted with unsaturated, especially alpha-beta-unsaturated, monocarboxylic acids or their derivatives at temperatures at which the amines are added on to the unsaturated monocarboxylic acids or their derivatives and amide formation between two or more molecules of the amino acids thus formed takes place. In the same application there is also described that the properties of the polyamides obtainable according to the said process may be varied either during or after their manufacture by reacting them with one or more organic compounds containing one or more groups capable of reacting with NH-groups. Among the compounds of the said type there are mentioned inter alia polycarboxylic acids.

We have now found that valuable condensation products can also be obtained by heating polyamides obtainable according to the process of the said application Ser. No. 252,630 or their said reaction products with organic compounds containing one or more groups capable of reacting with NH-groups, either during or after their manufacture, with superpolyamides, i. e. film-forming high molecular amides of polypeptide-like structure, as for example condensation products of diamines and dicarboxylic acids or of salts of diamines and dicarboxylic acids, and/or of aminocarboxylic acids or with the initial materials forming such superpolyamides.

In practicing the present invention the condensation products obtainable according to the process of the copending application Ser. 252,630 are, for example, melted together with the superpolyamides or the superpolyamides may already be added during the production of the condensation products according to application Ser. 252,630 or while they are reacted with a compound having one or more groups capable of reacting with NH-groups. Especially favorable results are obtained by carrying out the condensation according to application Ser. 252,630 in the presence of superpolyamide forming substances, as for example dicarboxylic acids and/or of ω -aminocarboxylic acids.

Dicarboxylic acids suitable for this reaction are in particular those of the formula



wherein x means a whole number greater than 3, for example adipic acid or sebacic acid, and also dicarboxylic acids interrupted one or more times by hetero atoms or groups containing hetero atoms, for example diglycollic acid, thiodipropionic acid, iminodipropionic acid or methyliminodipropionic acid. Mixtures of several dicarboxylic acids and salts of dicarboxylic acids with the diamines may also be used. Among suitable diamines there may be mentioned those of the formula $\text{NH}_2(\text{CH}_2)_x\text{NH}_2$, wherein x means a whole number greater than 3, for example tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, para-phenylenediamine, para-xylylenediamine, ω, ω' -diamino-para-diethylbenzene or their perhydrogenated derivatives. Diamines the carbon atoms of which are interrupted one or more times by hetero atoms, as for example oxygen or sulfur or groups containing hetero atoms, for example $-\text{SO}-$, $-\text{SO}_2-$ or $-\text{NX}-$ (X being hydrogen or a hydrocarbon radicle), may also be used. Among diamines of the latter kind we may mention for example beta-beta'-diaminodiethylether or -dipropylether and homologues thereof or similar thioethers. Mixtures of several of these amines may also be used.

As aminocarboxylic acids which may be heated with the condensation products obtainable according to application Ser. No. 252,630 there may be mentioned those of the general formula $\text{NH}_2(\text{CH}_2)_x\text{COOH}$, wherein x is a whole number preferably greater than 3, for example ϵ -aminocaproic acid. The carbon chain of amino acids, too, may be interrupted one or more times by the said hetero atoms or groups containing hetero atoms.

Instead of the free carboxylic acids, their functional derivatives, as for example their esters or amides, may also be employed undergoing the same reaction as the acids, save that alcohol or ammonia or an amine is split off instead of water.

The condensation may furthermore be influenced, especially the degree of condensation be varied, by the addition of small proportions of monocarboxylic acids, for example acetic acid, or of ammonia or monoamines, for example methylamine, dimethylamine, ethylamine, dipropylamine, octodecylamine, decylamine or also by

employing, the dicarboxylic acids or diamines in excess of the amount theoretically required for the interaction of both substances.

The condensation products are prepared by heating, preferably, at temperatures ranging between 100° and about 300° C. Depending on the temperature and the duration as well as on the method of heating, products of varying properties are obtained. Temperatures of more than 300° C should be avoided as they easily give rise to decomposition and darkening in color. The reaction may be carried out under ordinary, increased or reduced pressure. It is advantageous to employ at first increased pressure or to work with reflux cooling in order to thus bring the mass into as uniform as possible a state of melting, and then to complete the condensation under ordinary or reduced pressure while removing the resulting volatile constituents as water, alcohol, ammonia or amine by distillation. Solvents and/or diluents may be present, if so desired.

As solvents suitable in particular when free carboxylic acids are employed for the condensation may be mentioned such as form azeotropic mixtures with the water split off by the condensation, as for example xylene or xylenol. Generally speaking, it is most desirable to exclude air or oxygen as far as possible, in order to obtain products as colorless as possible.

The mixed high molecular condensation products of the superpolyamide type thus obtained are suitable for the manufacture of threads, films, ribbons, tubes, coverings, coatings, and moulded articles of a great variety of kinds. They are more plastic and softer than the pure superpolyamides from dicarboxylic acids and diamines or from aminocarboxylic acids. The condensation products from alpha-beta-unsaturated monocarboxylic acids and diamines having their amino groups separated from each other by at least 2 carbon atoms, obviously exert therein a softening or plasticizing effect. In contrast to softening and plasticizing agents otherwise employed for highly polymerized substances they have the great advantage of being chemically combined and, by reason of their high-molecular nature, being not subject to volatilization or dissolution.

The following Example will further illustrate how the present invention may be carried out in practice. The parts are by weight.

Example

A solution of 250.5 parts of an aqueous acrylic

acid of 71.8 per cent strength in 450 parts of alcohol is slowly added, while stirring, to a solution of 293 parts of hexamethylenediamine in 750 parts of alcohol and the mixture is boiled under reflux for 2 hours, whereupon the alcohol is distilled off under reduced pressure. The viscous yellowish oil thus obtained is heated with an equal proportion of adipic acid hexamethylenediamine salt for 90 minutes in a closed vessel at a temperature of from 275° to 280° C in the presence of nitrogen and then kept at this temperature for another 4 hours under atmospheric pressure. The condensation product thus obtained is extremely soft and flexible and eminently suitable for the manufacture of films.

The same reaction product is obtained by carrying out the reaction in only one stage, i. e. if the acrylic acid, adipic acid and the whole amount of hexamethylenediamine are mixed and then heated.

Instead of adipic acid hexamethylenediamine salt there may also be used the diglycollic acid hexamethylenediamine salt or mixtures of adipic acid and hexamethylenediamine or of diglycollic acid and hexamethylenediamine.

The ratio in which the condensation product from acrylic acid and hexamethylenediamine or the starting materials therefor and the adipic acid or diglycollic acid hexamethylenediamine salts may be combined with one another may be varied at will.

Using only from 10 to 20 per cent of the condensation product from acrylic acid and hexamethylenediamine and condensing the said product with adipic acid or diglycollic acid and hexamethylenediamine at from 210 to 220° C or even higher temperatures, for example at from 275 to 280° C, condensation products are obtained which are especially soft, flexible and solid. Instead of the only condensation product from acrylic acid and hexamethylenediamine, use may be made also of a solid crystalline product which may be obtained in the following manner.

A solution of 215 parts of acrylic acid methyl-ester in 750 parts of alcohol is slowly added at 25° C while stirring to a solution of 293 parts of hexamethylenediamine in 750 parts of alcohol. The mixture is further stirred at 70° for 5 hours, whereupon the alcohol is distilled off under reduced pressure.

HANNS UFER.
HANS SCHOENHERR.
AUGUST WEICKMANN.

ALIEN PROPERTY CUSTODIAN

PROCESS OF MANUFACTURE OF CELLULAR RUBBER HAVING FLUID-TIGHT CELLS

Louis Emile Henri Pagnon, Paris, France; vested
in the Alien Property Custodian

No Drawing. Application filed November 17, 1939

The present invention relates to a process for manufacturing cellular rubber having fluid-tight cells filled with a gas under pressure. It is known that, in all the present known processes, the mass of rubber, to which may optionally be added waxy or resinous materials and various fillers, is subjected in the hot state, in a fluid-tight receptacle, to the action of a gas at a high pressure, the value of which may reach 500 to 600 kg. at the end of the operation, said mass of rubber being thus simultaneously subjected to vulcanization and to the penetration of the gas which, so to speak, dissolves in the rubber and subsequently forms, at the instant when the free or controlled expansion takes place of the mass that has issued from the treating chamber, very fine cells which do not communicate with each other and are kept expanded by the residual pressure of the gas. This process offers the drawback of being very long and very expensive, and furthermore it does not produce sufficiently uniform products. In fact, on the one hand owing to the very high pressures at which it is necessary to make the gas penetrate into the mass of rubber, the fluid-tight receptacles in which this operation is effected have to have very thick walls, so that the heating of said receptacles (which is effected by means of an external circulation of steam), and also their subsequent cooling, takes a long time and involves a large consumption of heat; on the other hand, the mass of rubber being treated, which is enclosed in said receptacle, is not raised to a uniform temperature despite a very long duration of the treatment, so that the outer layers of the mass are vulcanized too much, whereas the central parts are not vulcanized enough. This in turn makes it impossible to treat a large quantity of rubber at one time, for example in the case of the manufacture of cellular rubber in slabs, the slabs of crude rubber are wound into rolls and treated in a cylindrical "shell", on a likewise cylindrical core of sufficiently large diameter to reduce the radial thickness of the layer of rubber through which the heat has to pass. Furthermore, in order to separate the convolutions which are wound on each other and to facilitate the propagation of the heat, it is necessary to wind a sheet of metal at the same time as the slab of rubber. For all these reasons, it is impossible in practice to treat more than 400 kg. of cellular rubber in slabs in the same apparatus; the treatment of such a weight requires about 24 hours, inclusive of cooling, and in spite of this duration and of the large consumption of heat, the slab obtained is not uniform, since its degree

of vulcanization varies substantially from one end to the other.

It has been proposed to overcome these drawbacks by previously subjecting the mass of rubber to heating, optionally accompanied by prevulcanization, and introducing the mass thus raised to the treating temperature into the fluid-tight receptacle, the walls of which have been previously raised to the requisite temperature. However, this process which above all offers the advantage of a more economical prevulcanization, does not enable the above drawbacks to be radically overcome, in particular the duration of the treatment and the consumption of heat to raise the apparatus to the required temperature and to maintain said temperature during the injection of the gas, and furthermore it is still difficult to obtain a homogeneous product owing to the difficulty of maintaining a uniform temperature throughout the entire mass. The duration of the treatment likewise remains long owing to the necessity of allowing the mass to cool in the fluid-tight receptacle.

The present invention has for its object a process which enables perfectly uniform products to be obtained, while considerably reducing the cost of manufacture and increasing the capacity of output of the apparatus. Said process is characterized by the fact that the prevulcanized mass of rubber is cooled and then subjected in the cold state to the action of the gas under pressure in the fluid-tight apparatus.

The inventor has in fact discovered that the penetration and the diffusion of the gas under pressure into a mass of rubber were in practice to a large extent independent of the temperature, and that the essential condition for the manufacture of a cellular rubber consists in the fact that, before being subjected to a free or controlled expansion, the mass of rubber containing the dissolved gas must be partly vulcanized, it being possible for such vulcanization to be effected before or during the injection of the gas.

The degree of prevulcanization effected before the injection of the gas under pressure is substantially the same in the process according to the invention as the degree of final vulcanization obtained in the usual processes, after the gas injection in the hot state.

The process according to the invention offers the very considerable advantage of not requiring any other supply of heat than that used for the prevulcanization, which is effected by the processes that are usual in the rubber industry and outside the fluid-tight apparatus for the

treatment with the gas at high pressure, and which can therefore be effected at small cost and with all desirable regularity. On the other hand, since the injection of the gas into the mass of rubber is effected in the cold state, the duration of this operation is reduced by the fact that it no longer necessitates heating the mass right through, or cooling after such heating. Similarly, the absence of heating during the injection enables the winding of a metal sheet with the slabs of rubber to be eliminated (a simple hooping with an outer metal sheet surrounding the roll is sufficient) and, furthermore, the diameter of the core on which said slabs are wound can be considerably reduced, thereby increasing the capacity of the apparatus. As a result of all these favorable factors, instead of producing 400 kg. of cellular rubber after a treatment of 24 hours, the process according to the invention enables 500 to 600 kg. of rubber to be treated in 12 hours in the same apparatus, while producing a final product of better quality. When it has been removed from the gas treatment chamber, the rubber is expanded in the usual manner, optionally in a finishing mould, with or without complementary vulcanization.

According to another feature of the present invention, the duration of the treatment with the gas under pressure is considerably decreased by the fact that the mass of prevulcanized and cooled rubber is successively or simultaneously treated with two gases under pressure, one of which has a great power of penetration and of diffusion, such as carbon dioxide, and is intended to act as a temporary inflation agent before leaving the mass by exosmosis owing to its great power of diffusion, and the other of which has a smaller power of penetration, such as nitrogen, and is intended to remain in the mass.

It is known in fact that the nitrogen that is generally used for the manufacture of cellular rubber is absorbed rather slowly by the rubber and in a quantity which does not exceed ten times the volume of the rubber at a fairly high pressure, of the order of 200 to 300 kg., and for a period which is compatible with industrial working. It is moreover this very difficulty of the diffusion of nitrogen in rubber that justifies its

use, since when it has penetrated into the mass and after its pressure inside the cells has been reduced by the expansion of the vulcanized rubber, the nitrogen has no tendency to escape therefrom. It is known, on the other hand, that carbon dioxide diffuses very readily in rubber, which can absorb in a few hours up to thirty five times its volume thereof, at a pressure of about 40 kg: on the other hand, owing to the ready manner in which it diffuses, carbon dioxide escapes from the rubber by exosmosis, so that after a few days, the cellular rubber obtained with this gas is completely deflated.

By making carbon dioxide and nitrogen act according to the invention, successively or simultaneously, each at a pressure which is best suited to it and the orders of magnitude of which have been stated above, on the one hand by means of the carbon dioxide a quick swelling at high pressure of the rubber mass is obtained which subsequently permits efficient expansion and efficient moulding, whereas on the other hand the nitrogen ensures a durable filling at low pressure of the cells that are expanded by the carbonic acid.

Furthermore, the time of absorption of the necessary volume of gas is thus reduced, the carbon dioxide appearing to favour the diffusion of the nitrogen that follows it, and furthermore this novel method of treatment requires substantially lower final pressures (200 to 300 kg. instead of 5 to 600). Although it can also be used in the known processes of gas injection in the hot state, this injection of two different gases is particularly advantageous in the case of the injection in the cold state according to the present invention, since in the first case, the total duration of the treatment chiefly depends on the duration of the heating and of the cooling, and not on the duration of the injection of the gas. The figures for the pressure have only been given by way of example; the pressures will be proportional to the dimensions of the work-pieces to be treated, to the nature of the mixtures (these being similar to the formulae acquired by experience of the usual processes), to the densities to be obtained, and to the periods of injection.

LOUIS EMILE HENRI PAGNON.

ALIEN PROPERTY CUSTODIAN

METHOD FOR THE MANUFACTURE OF CONDENSATION-PRODUCTS

Winfried Hentrich, Rodleben B. Dessau-Rosslau/
Anhalt, and Alfred Kirstahler, Dessau/Anhalt,
Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 21, 1939

It has been found that valuable condensation-products of the general formula $R.X.N(G)Y.R'$ are obtainable in condensing—in a way known in itself—acid-halogenides of the general formula $R'.Y.Hal$ with acid-amides of the general formula $R.X.NH_2$ or their metal-compounds respectively and in converting the thus obtained condensation-products with alkylene-oxides. In the said formulae R and R' means any homogeneous or unhomogeneous organic residues, X and Y the groups SO_2 and CO ; Hal a halogen atom and G a residue formed by an addition of alkylene oxides.

The organic residues R and R' of the general formula may belong to the aliphatic, cycloaliphatic, aromatic or heterocyclic series or mixed types of these series; they may eventually contain hetero-atoms or hetero-atom groups such as halogen, oxygen, sulfur, nitrogen, hydroxyl-keto-, ester-, sulfo-, amino-, alkylamino-, acylamino-, sulfimide-, inorganic and organic acid groups and the like.

Those residues may be e. g. methyl-, ethyl-, butyl-, hexyl-, octyl-, dodecyl-, oleyl-, ricinoleyl-, montanyl residues and the like, furthermore any ramified residues such as isohexyl-, iso-dodecyl-, iso-octadecyl residues and the like.

As cyclic hydrocarbon residues there may be considered the cyclo-hexyl residue, cyclohexyl residues substituted in the nucleus by any alkyl residues, the naphthenyl-, abietyl-, benzyl-, tetrahydro-menaphthyl residue, phenyl-, naphthyl-, anthrazyl residues, phenyl- or naphthyl residues substituted in the nucleus by any alkyl- or cyclo-alkyl residues, pyridine- and quinoline-residues and the like.

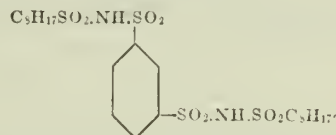
As initial stuffs for the present method we may consequently apply e. g. the halogenides or amides of the following sulfonic acids: octyl-sulfonic acid, dodecyl-sulfonic acid, cetyl-sulfonic acid, octadecyl-sulfonic acid, p-dodecylamino-benzol-sulfonic acid, p-octadecyl-hydroxy-benzol-sulfonic acid, alkylated naphthalene- and tetrahydronaphthalene-sulfonic acids, furthermore methyl-sulfonic acid, n-butyl-sulfonic acid, propan-1,3-disulfonic acid, cyclohexyl-sulfonic acid, benzyl-sulfonic acid, toluol-4-sulfonic acid, chlorobenzol-4-sulfonic acid, benzol-1,3-disulfonic acid, naphthalene-1-monosulfonic acid, -1,5-disulfonic acid or -1,3,6-trisulfonic acid respectively, dimethyl-aniline-p-sulfonic acid and the like.

In a corresponding manner we may apply the halogenides and amides of the following carbonic acids: acetic acid, butyric acid, lauric acid, oleic acid, montan acid, adipic acid, naphthenic acid,

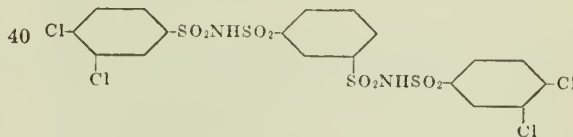
abietic acid or other resinic acids, benzoic acid, phthalic acid, cyclohexane-di-acetic acid, pyridine-carbonic acids and the like.

The converting among the initial stuffs is performed according to methods known in themselves either directly or in the presence of an indifferent diluent such as benzine, chloro-hydrocarbons, benzol and the like, whereby sulfimides as well as carbimides or also mixed acid-imides may be developed. The acid-amides are preferably applied in the form of their metal—and particularly of their alkali-metal compounds. But we may likewise work with the free acid-amides and eventually in the presence of acid-binding agents. Instead of the acid-halogenides we may also use any other functional derivatives of those acids such as acid-anhydrides.

Condensation-products obtained in this way are e. g. the methyl-n-dodecyl-sulfimide, di-octyl-sulfimide, p-toluol-dodecyl-sulfimide, m-carboxylphenyl-dodecyl-sulfimide, hexadecyl-benzyl-sulfimide, octadecyl-cyclohexyl-sulfimide, p-dodecyl-amino-benzol-methyl-sulfimide, bis-(n-octyl-sulfo)-1,3-phenylene-disulfo-di-imide of the formula



furthermore hexadecyl-octyl-sulfimide, octadecyl-cyclohexyl-sulfimide, tetradecyl-benzyl-sulfimide, di-p-toluol-sulfimide, 3,4-dichlorobenzol-benzyl-sulfimide, 3-nitro-benzol-4'-methyl-benzol-sulfimide, bis-(4', 3'-dichloro-benzol-sulfo-) 1,3-disulfo-benzol-di-imide of the formula



N-acetyl-, N-isobutyryl-, N-lauroyl-benzol-sulfamide, N-oleoyl-toluol-sulfamide, diacetamide, dipropionamide, dibenzamide, N-lauroyl-benzamide, N-acetyl-toluyl-amide and the like.

Those condensation-products corresponding to the present invention are now treated with alkylene-oxides. Such alkylene-oxides are e. g. ethylene-oxide, 1,2-propylene-oxide, 1,2-butylene oxide, 1,2-cetene-oxide, glycid, epi-chlorhydrine, cyclohexene-oxide, methyl-cyclo-hexene-oxide and the like. With this reaction condensation-

products are developed with an oxalkyl-group or with poly-ether-groups respectively, which are then of a particular technical value in letting the alkylene-oxides react in excess upon the imides, because we thus are in a position of obtaining the solubility of the total molecule in water. If in this case the imides contain lipophile residues i. e. at least one higher molecular hydrocarbon residue of no less than 6 C atoms, we come to stuffs with capillary active properties, which are therefore of a particular technical value.

The reacting of the alkylene oxides may be performed in quantities of 1 to 25 mols and more. According to the size of the molecule of the imide we preferably apply quantities of 6 to 15 mols. The reaction may be enhanced especially by basic stuffs such as caustic alkalis and alcohols as well as by phenolates or we may likewise employ the salts—and especially alkali salts—of the imides themselves.

The products obtained according to the present method may serve as softening means and plasticizing means for cellulose-derivatives, artificial stuffs e. g. of the poly-vinyl series, natural or artificial cautchouc and the like. As far as the products are capillary active they show excellent wetting-out-, emulsifying-, dispersing-, washing- and deterging properties and they are therefore valuable soap-substitutes because of their real colloidal character. Owing to this quality they are advantageously used in the leather-, fur- and textile industries as well as in laundries.

The alcoholic hydroxy-groups developing in the converting with the alkylene-oxides may eventually be converted with reactive compounds e. g. while forming esters with poly-basic inorganic or organic acids or with their functional derivatives such as sulfuric acid, phosphoric acid, boric acid, sulfo-acetic acid, sulfo-succinic acid, sulfo-phthalic acid, halogen fatty acids, whereat a further improvement of the products may be obtained for certain applying-purposes and especially an enhancement of the solubility in water.

Example 1

11,4 weight-parts of methyl-sulfochloride and

35,5 weight-parts of octa-decyl-sulfamide-sodium are boiled at the reflux-cooler for several hours and in the presence of 120 weight parts of toluol. After distilling-off the solvent the residue is treated with a hot and very diluted soda-solution, whereupon we filter off from any unsolved particles. The thus formed condensation-product is then separated from the filtrate with mineral acids. There remains a fatty to wax-like substance of the formula $\text{CH}_3\text{SO}_2\text{NH}\cdot\text{SO}_2\text{C}_{18}\text{H}_{37}$.

41 weight parts of this condensation-product are treated in the autoclave with 53 weight parts of ethylene-oxide while stirring at 120 to 130° C and in the presence of 1% of caustic soda. The heating is continued till the pressure has practically ceased. The thus obtained condensation-product is a viscous water-soluble mass which supplies lathering aqueous solutions. In an analogous manner we obtain the reaction-product of ethylene-oxide on di-n-octyl-sulfo-imide, which is likewise soluble in water.

Example 2

23,7 weight parts of lauric acid chloride and 19,5 weight parts of benzol-sulfamide-potassium are condensed as per example 1) by boiling at the reflux-cooler in the presence of toluol. We thus obtain, after working-up, the condensation-product of the formula $\text{C}_{12}\text{H}_{25}\text{CO}\cdot\text{NH}\cdot\text{SO}_2\text{C}_6\text{H}_5$ in the form of a white mass. 35,3 weight parts of this product are treated as per example 1) in the autoclave with 30 weight parts of ethyl-oxide. 39,7 weight parts of the thus obtained additive product of the formula



are sulfonated with 12,5 weight parts of chloro-sulfonic acid in the presence of 50 cm³ of ether at 5 to 15° C. Then we continue stirring for a little while at room temperature till a sample proves soluble in water, whereupon we neutralize with a 33%-sodium lye. The reaction-product is worked up in the usual way and in aqueous solutions it shows soap-like properties.

WINFRID HENTRICH,
ALFRED KIRSTAHLER.

ALIEN PROPERTY CUSTODIAN

NOVEL CHROMIFEROUS DYESTUFFS AND PROCESSES FOR MAKING THE SAME

Georges Kopp and Jean Henri Meybeck, Rouen, France; vested in the Alien Property Custodian

No Drawing. Application filed November 21, 1939

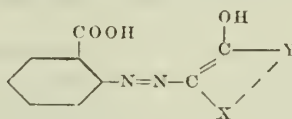
In the U. S. A. Patent N° 2.133.864 the existence of two kinds of chromiferous ortho-oxyazoic complexes has been pointed out, the ones of which are preferably formed in a neutral medium and will be called hereafter "primary chromium compounds," while the others are formed in an acid medium and will be called hereafter "secondary chromium compounds." In the above mentioned patent are described processes which permit to obtain, at will and in each case, the so-called "primary" and "secondary" complexes. The dyestuffs which are mentioned in this patent are exclusively ortho-oxy-azoic dyestuffs derived principally from orthoamidophenols and orthoaminophenols.

Now it has been found, according to the present invention, that the orthocarboxyazoic dyestuffs derived from orthoaminocarboxylic acids also lead to two kinds of chromiferous compounds, the ones of which are preferably formed in a neutrol medium, while the others are exclusively formed in a strongly acid medium. However it will be noted that whilst most of the ortho-oxyazoic dyestuffs already form secondary complexes in a weakly acid medium, in the case of the orthocarboxyazoic dyestuffs the secondary complexes are more particularly formed in a strongly acid medium. The differences in the properties of the primary and secondary complexes are generally very marked. In all the cases the secondary complexes are brighter and unite remarkably well on wool in an acid bath, while the primary complexes unite so badly that their commercial use is in most cases excluded. Another advantage of the secondary complexes is the possibility of rapidly dyeing them in a weakly acid bath, while the primary complexes require high quantities of acid and very long durations of the dyeing operation.

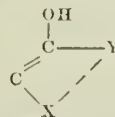
Although some chromium complexes of o-carboxyazoic dyestuffs have already been obtained in an acid medium the possibility of producing two kinds of ortho-carboxy-azoic chromium complexes was not hitherto known. It is said, for instance, in the French Patent N° 758.263 of July 12, 1933, in Example 2: Dyestuffs having similar properties are obtained when the chromidization is effected with other chromium salts." But the process of this example leads to the pure primary complex without any trace of secondary complex; the latter which, moreover, forms only in a chroming medium which is clearly acid to Congo red, dyes the animal fibres in a weakly acid bath in perfectly uniform golden yellow, while the pri-

mary complex used in the same conditions gives a very unequal yellow-orange tint.

More particularly it has been ascertained according to the present invention, that novel complexes of a high commercial interest are obtained by subjecting to the action of agents which are acid to Congo red, at a high temperature, the chromium complexes of the dyestuffs of the general formula



15 in which



represents the rest of a sulphonated arylpyrazolone, of a sulphonated naphthol or of a sulphonated arylide of acylacetic acid.

The dyestuffs which can be used as starting materials for carrying out the invention can be obtained by diazotation of the anthranilic acid and copulation of the obtained diazoic derivative with a sulphonated arylpyrazolone, a sulphonated naphthol or a sulphonated arylide of acylacetic acid; the above mentioned copulating agents may contain a plurality of SO₂H groups and other substituents such as halogen atoms, the alkyl, alkoxy, carboxy, sulphamido groups and the like; they can also be obtained by sulphonation of non-sulphonated monoazoic compounds.

The secondary chromium compounds according to the invention can be obtained in one or more steps.

It is more particularly possible to first produce the primary compound in the absence of strong mineral acid and to convert this compound into a secondary complex. This conversion can be effected in the medium in which the production of the primary one has been effected or in another medium after isolation of the primary compound; it is sufficient to heat the chromium complex in the presence of any acid product such as sulphuric, hydrochloric, arylsulphonic acid or the like, in a sufficient quantity in order that the reaction mixture gives a clearly blue coloration with Congo red.

It is also possible to heat the orthocarboxyazoic dyestuff with a chromium salt in such conditions that the reaction is strongly acid at least at the end of the chroming treatment. This work-

ing method can be performed through the addition of any acid product in a sufficient quantity in order that the reaction mixture gives a clearly blue coloration with Congo red; it can also be performed by using as a chroming agent a chromium salt such as chromium sulphate and the arylsulphonates of chromium which give a sufficient acidity during the chroming treatment.

In certain cases even very small quantities of water soluble saline materials can retard the formation of the secondary complexes; in order to avoid this draw-back the starting dyestuffs are completely freed from saline materials by converting the said dyestuffs by any means into free acids; the obtained products are then subjected to the action of chroming agents in a medium which is acid to Congo red, as above mentioned.

The production of sulphonated azoic dyestuffs which are free from salts and in the state of free acids can be effected, in some cases, by treating alkaline salts with strong excesses of mineral acids. This process gives satisfactory results when the free acids are little soluble in the presence of an excess of mineral acid, but it can be used only if the reaction of the mineral acid with the dyestuff can be performed in such conditions that the mineral acid effectively displaces the free acid of the dyestuff. Another more general process consists in precipitating the dyestuffs in the form of earth-alkaline salts and in treating the so formed salts by sulphuric acid; thus an insoluble earth-alkaline sulphate and a dyestuff in the state of free acid are formed. The chromating operation can be effected either in the presence of the insoluble sulphate or after elimination of the latter, for instance in the cases in which the free acids of the dyestuffs are soluble in water.

The process according to the invention applies as well to the pure dyestuffs as to their mixtures eventually with dyestuffs which do not correspond to the above given definition.

The formation of the secondary complexes takes place in various conditions of temperature, volume and pressure.

The secondary orthocarboxyazoic chromiferous complexes according to the invention can be used for the coloration of fibres of all kinds such as wools, artificial protein fibres, leathers, hides and the like. Certain of these chromiferous complexes are soluble in organic solvents and can be used in the manufacture of varnishes, plastic materials, fatty bodies and the like.

The following examples of execution of the invention are given by way of non-limiting examples.

Example 1

40.4 parts of the monosodic salt of the azoic dyestuff obtained by copulation of the 2-diazo-benzene-1-carboxylic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are dissolved in 500 parts of water, and 20 parts of chromium formate are added and the whole is heated on reflux during several hours. The primary chromiferous complex obtained which is very soluble, is isolated by salting out. It dyes the wool in an acid bath in rather dull reddish yellow with the disadvantage of uniting very badly.

When subjected in the boiling state to the action of diluted mineral acids this product gives a novel chromium compound, i. e. a secondary compound which is little soluble in water.

This secondary complex can be directly produced by heating on reflux during several hours 40.4 parts of the azoic dyestuff described in the

first paragraph of this example with 500 parts of water, 7.8 parts of Cr_2O_3 in the form of a solution of chromium sulphate and 11.5 parts of sulphuric acid of 36° Bé. The chromiferous complex, which is little soluble, precipitates as it is formed in the form of splendid crystals. It is separated by filtration. When converted into a sodium salt it dyes the wool in an acid bath in a bright yellow tint which is very well united and possesses excellent properties of solidity.

Example 2

37.3 parts of the monosodic salt of the dyestuff obtained by copulation of the 2-diazo-benzene-1-carboxylic acid with the naphthol-sulphonic-1.5 acid, are dissolved in 500 parts of water and 11.5 parts of sulphuric acid of 36° Bé and 7.8 parts of Cr_2O_3 in the form of a solution of chromium sulphate are added. After having heated on reflux during several hours, the secondary compound begins to precipitate in the form of bright crystals; heating is still continued during 6 to 8 hours and the dyestuff is separated by filtration. When converted into a sodium salt it dyes the wool in an acid bath in a bright violet tint which unites very well and has excellent properties of solidity. The primary compound which can be readily obtained by performing the chroming operation in a neutral medium with formate or acetate of chromium, for instance, possesses dyeing properties of much less interest; it dyes the wool in an acid bath in a brownish violet tint which is dull and unites very badly.

The secondary compound also differs from the primary compound by the following reactions:

The aqueous solutions of the sodium salts show different changes in the contact of the following chemical agents:

	HCl 10°	NaOH 5%
Primary	Violet grey.	Orange grey.
Secondary compound	Bord aux.	Orange.

The colorations of the solutions in concentrated sulphuric acid are as follows:

Primary compound..... Brown
Secondary compound..... Bottle green

Example 3

35 parts of the monosodic salt of the dyestuff resulting from the copulation of the 2-diazo-benzene-1-carboxylic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are heated on reflux with 200 parts of water, 15 parts of chromium fluoride, 8 parts of pyridine and 15 parts of sulphuric acid of 36° Bé. After a few hours the formation of bright crystals is observed which are constituted of the secondary chromium complex which after being filtered and transformed into an alkaline salt dyes the wool in an acid bath in a perfectly united golden yellow.

The same reaction when made in the absence of sulphuric acid very rapidly leads to the primary complex which dyes the wool in a reddish yellow of very bad union and which, therefore, is of no practical interest.

Example 4

10 parts of the monosodic salt of the dyestuff resulting from the copulation of the 2-diazo-benzene-1-carboxylic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are treated with 1000 parts of boiling water and a quantity of hydrochloric acid which is sufficient for

acidifying; then is added a solution of 15 parts of crystallized barium chloride in 100 parts of water. The barium salt of the dyestuff crystallizes and is isolated by filtration and then converted into free acid by a treatment with diluted sulphuric acid and elimination of the barium sulphate. 100 parts of a solution of basic chromium sulphate containing 15% of $\text{Cr}(\text{OH})_3$ are added to the solution of free acid, the whole is heated on reflux until total conversion into a secondary chromium complex which crystallizes in the form of large scales having a metallic glow, then it is filtered and converted into a soluble alkaline salt. The novel dyestuff dyes animal and artificial fibres containing protein substances in a golden yellow having excellent properties of solidity.

Example 5

37.3 parts of the dyestuff resulting from the copulation of the diazotated anthranilic acid with the 1-naptol-5-sulphonic acid are dissolved in 500 parts of water; 10 parts of hydrochloric acid and 15 parts of crystallized barium chloride are then added. The barium salt obtained is isolated and converted into a free acid by means of sulphuric acid. 10.3 parts of chromium hydroxide and 15 parts of sulphuric acid of 36° Be are added to this product and the whole is heated on reflux until complete crystallization, filtered and converted into a sodium salt. The novel dyestuff dyes the animal fibres in an acid bath in violet colour.

Example 6

40.4 parts of the monosodic salt of the dyestuff resulting from the copulation of the diazotated anthranilic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are dissolved into 1600 parts of water and 10 parts of pyridin. 15 parts of chromium fluoride are then added and the whole is heated on reflux. After having been heated during a few hours the dyestuff is completely converted into a chromium complex of the primary type. A continuation of the heating operation does no longer change the properties of this complex which can be isolated by salting or by evaporation in a dry state. This dyestuff,

which is very soluble in water, dyes the wool in an acid bath in reddish yellow of very bad unison. It can be converted into a complex of the secondary type in the following manner:

5 The dyestuff resulting from the application of the above described process is dissolved in 800 parts of water and 15 parts of sulphuric acid of 36° Be are added; then it is heated on reflux during several hours. The formation of crystals is observed which show a bronzed glow and are isolated by filtration. They are formed of secondary chromium complex in the state of a free acid. When converted into a soluble alkaline salt, the novel chromiferous complex dyes the wool in an acid bath in a perfectly uniform clear yellow.

Example 7

20 The process of example 5 is applied to the dyestuff obtained by copulation of the diazotated anthranilic acid with the naphthol-2-sulphonic-6 acid. The obtained secondary compound gives aqueous solutions of a bright yellowish red colour and dyes the animal fibres in an acid bath in unalterable red.

25 This novel process permits to obtain a rather complete range of valuable chromiferous dyestuffs. The anthranilic acid gives by diazotation, copulation and chroming in a strongly acid medium dyestuffs the colours of which vary according to the copulating agents. The shades which are obtained with various copulating agents are as follows:

Copulating agents	Tint of the dyeing on wool in an acid bath
35 Sulphonated acylacetic arylides and their substitution products.	Greenish yellows.
Sulphonated pyrazolones and their substitution products.	Clear yellows.
40 Beta-naphthol-sulphonic acids in which position 1 is free.	Clear reds.
Alpha-naphthol-sulphonic acids copulating in position 2.	Bordeaux and violets.

45
GEORGES KOPP.
JEAN HENRI MEYBECK.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF CELLULAR RUBBER HAVING FLUID-TIGHT CELLS

Louis Emile Henri Pagnon, Paris, France; vested
in the Alien Property Custodian

No Drawing. Application filed November 25, 1939

The present invention relates to a process for the manufacture of cellular rubber having fluid-tight cells. It is known that this product can be manufactured by vulcanizing a mass of rubber in the presence of a gas at a very high pressure, of the order of 300 to 600 atmospheres, and then subjecting the product thus obtained to a second vulcanization, at a temperature equal to or greater than that of the first, in a finishing or expansion mould in which the rubber having fluid-tight cells filled with gas assumes its final dimensions by expanding. However, there exists another process according to which this expansion of the vulcanized mass containing the gas under pressure is not effected in a mould at high temperature, but by simply staying in hot water or in hot air at a much lower temperature than the vulcanization temperature, for example of the order of 80° C. Nevertheless it has been observed that when this latter process was applied to a mass solely composed of plantation rubber to which had simply been added the products required for the vulcanization, a stable product having really fluid-tight cells was not obtained, so that the cellular rubber thus manufactured would not retain the gases. In order to overcome this drawback, up to 50% of balata gum and also waxy and resinous substances are mixed with the crude plantation rubber, which has the effect of closing the cells. However, balata gum is an expensive substance which is rather irregular in quality and is often difficult to obtain.

The purpose of the process which is the object of the present invention is to eliminate the use of balata gum in the mixture used for the manufacture of cellular rubber; it is characterized by the fact that a part of the mixture of pure gums used for this manufacture is subjected to a pre-treatment, the purpose of which is to decrease or to delay the effects of the vulcanization on this part of the mixture, the result of which is that in the finished product, said part of the mixture remains more plastic, whereas the remainder is more resilient.

The inventor has discovered in fact that the plasticity of the part of the mixture in which vulcanization was delayed was sufficient to permit of a subsequent expansion of the cells without breaking down their walls, whereas the part of the mixture formed by rubber which has been subjected under the same conditions to a much more complete vulcanization, imparted the required elasticity to the final product.

The pre-treatment applied to a part of the mixture used for the manufacture of cellular rubber, in order to retain the plasticity of said part in the final product, is based on the known fact the capacity of rubber for vulcanization depends on its state of polymerization and that the more completely the rubber is depolymerized, the longer

has to be the vulcanization to obtain the same result, whereas for the same time of vulcanization, a more complete depolymerization produces a decrease in the modulus of elasticity and therefore a less resilient and more plastic product. According to the invention, it is therefore possible to subject a part of the rubber forming the mixture to any treatment which is capable of decreasing its natural elasticity by depolymerization, and such treatment may be mechanical or chemical.

The desired result may be obtained in particular by subjecting crude plantation rubber to an operation of mixing, or of premastication, of long duration in a mixer provided with cooled cylinders which are kept at a temperature of the order of 20 to 30° C. For example, a mixture of gums may be used comprising 50% of plantation crepe that has been subjected to mixing for about 1 hour 45 minutes, and 50% of smoked sheets that have been subjected to mixing for only 30 minutes, these two components being then mixed by means of a mixing operation of about 10 minutes followed by the introduction of the fillers and of the vulcanizing agents.

The plastification of the rubber may also be obtained by means of a mastication operation of relatively short duration, but at a high temperature, of the order of 200° C.

This result may again be obtained without mechanical work, by simply oxidizing the crude rubber which, in this case is cut in pieces and dried in the hot state in vacuum drying ovens and then suddenly placed in the presence of air from which it absorbs the oxygen, thereby effecting the depolymerization and producing an equivalent result to the plastification obtained mechanically.

It is also possible to use as the plastic component of the mixture used for the manufacture of cellular rubber according to the invention, a natural or synthetic rubber which has been subjected to various chemical treatments that have the effect of imparting to it as regards vulcanization the some properties as those of considerably depolymerized rubber, for example chlorinated, brominated, hydrogenated rubber or the like, or again synthetic rubbers specially prepared so as to impart to them a low capacity for vulcanization.

The process according to the invention enables the cost of manufacture of cellular rubber to be substantially decreased, owing to the elimination of the use of balata gum or of gutta percha, and, by expansion in hot water or hot air of the mass that has been vulcanized in the gas under pressure, a product to be obtained which is equivalent to that obtained by expansion at high temperature in a finishing mould. However, a mixture of rubber treated according to the present invention can also be successfully used in this latter case.

LOUIS EMILE HENRI PAGNON.

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ALIEN PROPERTY CUSTODIAN

METHOD FOR PREPARING CONDENSATION PRODUCTS OF THE TYPE OF THE FURYL-METHANE DERIVATIVES

Piet Cornelis Kruyff, Woerden, The Netherlands;
vested in the Alien Property Custodian

No Drawing. Application filed November 28, 1939

This invention relates to a method for preparing condensation products of the type of the furylmethane derivatives.

Organic compounds having a hydroxyl or amino group can be condensed with aldehydes, for instance phenols can be condensed with formaldehyde, acetaldehyde, benzaldehyde, furfural and hydroxymethylfurfural, and in many cases the condensation can be satisfactorily carried out in an acid medium. Where compounds of the type of furfural and hydroxymethylfurfural are being treated in an acid medium, however, there is a tendency for non-uniform products to be obtained and for undesirable side reactions to take place. For instance, hydroxymethylfurfural shows a tendency to form laevuline acid and formic acid by opening of the ring and to form complex compounds of the type usually called humus substances.

Furane derivatives can also be formed from carbohydrates by the action for instance of phloroglucinol and hydrochloric acid or resorcinol and hydrochloric acid, according to the method of Seliwanoff or Fiehe, and methods of detecting pentoses and hexoses exist based on such reactions, which involve the intermediate production of a furfural body from the carbohydrate. However, it can be seen from *Berichte* 37, 304 (1904), *Zeitschrift für Analytische Chemie* 66, 134-7, *Cellulose Chemie* 6, 61 and 81 (1925), and the textbook "Chemie der Zellulose" by K. Hess that the normal condensation product of hydroxymethylfurfural with for instance phloroglucinol is only partly soluble in alcohol and is not a homogeneous substance. This is true whether the hydroxymethylfurfural is formed from a sugar in the reaction or is a pure substance previously prepared, and it seems that the hydroxymethylfurfural is partly decomposed in side reactions, leading, for instance to the formation of humus substances.

This invention is concerned with a method of producing, from carbohydrates and organic compounds (especially aromatic compounds) having one or more free or substituted hydroxyl or amino groups, good yields of relatively homogeneous condensation products.

It has now been found that when forming condensation products of the furylmethane derivative type in this way in the presence of an acid, improved results are obtained if the reaction is carried out in the presence of such a quantity of the said organic compound that an excess of this compound relative to the furfural body is present throughout the reaction.

As indicated above, the first stage of the reaction consists in the formation of a furfural body from the carbo-hydrate, this furfural body then condensing with the organic compound having one or more free or substituted hydroxy or amino groups (which compound may be introduced as such or in solution) and the rate of formation of the furfural body in the first stage of the process depends upon such considerations as the temperature and the quantity of acid used and its nature. The higher the temperature and the greater the quantity of acid the faster is the furfural body formed. Suitable acids are the mineral acids, including sulphuric acid, hydrochloric acid and phosphoric acid, and strong organic acids, e. g. phenol sulphonic acid. Acid compounds such as phosphorous oxychloride (POCl_3) are suitable, and are included in the term "acid" in the preceding paragraph. Mixtures of acids can be used.

In order to obtain as high a yield of the furylmethane derivative as possible care should be taken that there is no local formation of too much of the furfural body relative to the organic compound with which it is to be condensed, which would reduce the excess of this organic compound locally, and hence homogeneous conditions throughout the reaction mixture are desirable. There is then little loss of the furfural body by undesirable side-reactions.

One way of ensuring that the required excess of the organic compound containing one or more free or substituted hydroxy or amino groups is always present is to introduce at the beginning of the reaction so much of the organic compound that an adequate quantity of it remains at the end of the reaction. Another way is to carry out the reaction in such a manner that the relative proportions of the furfural body and the said organic compound present in the reaction mixture remain approximately the same as the reaction proceeds, this proportion being such that the desired excess of the aromatic compound is present. The rate at which the furfural body is formed depends upon the ratio of the acid to the carbohydrate, and in the second of the above two cases the amount of the organic compound present with which the furfural body is to be condensed therefore depends upon this ratio.

Examples of carbohydrates which may be used are sucrose, glucose, mannose, dextrine and starch and mixtures of these, and the hexoses and polyhexoses (i. e. di and polysaccharides containing hexose units) are especially suitable. Other carbohydrates can, however, be employed

provided of course that they can be converted into furfural bodies. It must be remembered that all the carbohydrates do not change to the furfural bodies at the same speed, and this must be taken into consideration in calculating the excess of the organic compound which must always be present during the reaction.

The organic compound containing one or more free or substituted hydroxy or amino groups may, for instance, be an aromatic or hydro-aromatic substance, e. g. phenol, resorcinol, phloroglucinol or dimethylhydroaniline, or may be an aliphatic substance, for instance mannitol or other polyalcohol.

The invention is illustrated by the following examples.

Example 1.—4 gram molecules of resorcinol are dissolved in 25 - 35% hydrochloric acid or 30 - 35% sulphuric acid. 1 gram molecule of fructose or glucose is then added in very finely powdered form to the solution in the cold and is dissolved with continued stirring. The solution is then heated to 50 - 90° C, when a red solid gradually separates. This substance appears to be a diphenyl furylmethane compound formed from two molecules of the resorcinol with one molecule of hydroxymethyl-furfural which has been formed by the action of the acid on the sugar, which seems to be converted almost quantitatively into the diphenylfurylmethane compound. The solid substance is then filtered off and washed.

The product appears to be completely soluble in alcohol or acetone, but not in benzene, and is also soluble in aqueous inorganic bases. It can be converted into a resinous substance of the thermo-setting type by condensing it with formaldehyde in the presence of an alkali or with hexamethylenetetramine. The product can also be careful sulphonation be converted into a water-soluble compound suitable for use as a tanning substance in tanning leather and as colouring means for use with cotton and other materials.

Example 2.—0.5 to 0.75 or 1 gram molecule of concentrated sulphuric acid of specific gravity 1.84 is added to 4 to 8 gram molecules of phenol. The mixture is heated to a temperature between 110 and 170° C with continued stirring and 1 gram molecule of glucose in finely powdered form is gradually added in small quantities. The mixture is then kept for one to two hours at the selected temperature with continued stirring, and the acid concentration indicated above ensures a sufficiently rapid reaction. Water vapour and phenol vapour evolved can be condensed in the usual way. On completion of the reaction the excess of phenol is removed, for instance by extraction with benzene, and the reaction product is washed free from acid by means of water.

The product appears to have been formed in the same way as indicated in Example 1, two

molecules of phenol having condensed with one molecule of hydroxymethylfurfural which has been formed almost quantitatively from the carbo-hydroxide. The product has similar properties to that of Example 1.

Example 3.—A reaction product similar to that of Example 2 can be obtained under conditions similar to those described in Example 2 by adding 1 gram molecule of sucrose to a mixture at least 5 gram molecules of phenol and a quantity of concentrated sulphuric acid, for instance 0.05 to 0.1 gram molecules.

Example 4.—Under reaction conditions similar to those described in Example 2, one gram molecule of very finely powdered fructose is added at a temperature of 110-120° C to 8 gram molecules of phenol and a quantity of sulphuric acid, for instance one third gram molecule.

The purified reaction product has properties similar to those of the products of Examples 1 to 3.

Example 5.—In this example, phenol sulphonic acid previously prepared is used instead of a mixture of phenol and sulphuric acid. Thus the carbohydrate, e. g. glucose or sucrose, can be gradually added in a very finely powdered form to the phenol sulphonic acid at a temperature of 110 to 120° C, or there may be added to the phenol sulphonic acid first a quantity of phenol and then, at 110 to 170° C, the finely powdered carbohydrate, in small quantities.

Example 6.—20 grams of phosphorous oxychloride (POCl_3) are mixed with 100 grams of dimethylaniline and 18 grams of sucrose or glucose in a very finely powdered form are very gradually added to the mixture. On completion of the reaction the acid is neutralized, the excess of dimethylaniline is removed, for instance by steam distillation, and the reaction product is dried.

The product is completely soluble in dilute acids and in alcohols, acetone and other solvents. The product is analogous to the leucobases of malachite green, and by careful oxidation in for example an acid medium can be converted into a dark blue pigment of high colouring power.

Example 7.—Example 6 is repeated, except that 100 grams of dimethylhydroaniline are used instead of the 100 grams of dimethylaniline, and 20 grams of phosgene are used instead of the 20 grams of phosphorous oxychloride.

Example 8.—1 gram molecule of hexose or 0.5 gram molecule of sucrose in finely ground condition is very gradually added to a mixture of 6 gram molecules of mannitol and 0.1 to 0.5 gram molecules of sulphuric acid, at a temperature of 160 - 170° C.

The reaction product is a resinous substance completely soluble in the usual solvents and substantially free from humus substances.

PIET CORNELIS KRUYFF.

ALIEN PROPERTY CUSTODIAN

RUBBER-LIKE MATERIALS FROM DI-HYDROXYALKYL SULPHIDES

Tadao Okita, Imazucho, Nishinomiya, Japan;
vested in the Alien Property Custodian

No Drawing. Application filed November 29, 1939

The present application is a continuation in part of my prior copending application Serial No. 94,194, filed August 4, 1936, for "Rubber-Like Materials from Di-Hydroxyalkyl Sulphides."

The present invention relates to the method of manufacturing rubber-like materials under ordinary temperature or heating and with or without solvent, of concentrated sulphuric acid, phosphoric acid, arsenic acid, boric acid anhydride, potassium bisulphate, zinc chloride, tin chloride and other metallic halogenides or ammonium chloride reacted upon the materials which are expressed by $[(HO)C_nH_{2n}]_2S_x$ (where n and x are positive integers in this case).

The object of the present invention is an economical manufacture of the rubber substitutes

Oil-proof rubber-like materials have hitherto been manufactured mainly by the working of saturated halogenide of hydrocarbon of a rather low molecular weight in water or in alkaline solvent upon the materials generative of sulphur such as alkali sulphides or alkaline earth metal sulphides, but the operation has not only been difficult but economically disadvantageous.

The present invention shows the method of manufacturing elastic rubber-like materials under ordinary temperature or heating and with or without solvent, of concentrated sulphuric acid, phosphoric acid, arsenic acid, boric acid anhydride, potassium bisulphate, zinc chloride, tin

chloride and other metallic halogenides such as mercury chloride, calcium chloride, boron fluoride or ammonium chloride upon the chemicals which are expressed by $[(HO)C_nH_{2n}]_2S_x$ (where n and x are positive integers in this case). For example, by heating at 150°C for an hour the mixtures of 100 grams of dihydroxyethyl disulphide and 100 grams of concentrated sulphuric acid, about 80 grams of rubber-like material can be obtained, which is of great elasticity and oil-proof property, and also of far less offensive odor than the one manufactured from ethylene chloride.

In practising my invention the integer n should be chosen between 1 and 6 (and preferably between 2 and 5) while the integer x should be chosen between 2 and 4. It will be understood that whenever an integer is herein defined as being between two limiting numbers the range of values of such integer is to be taken as including both the limiting numbers.

Although I have shown and described certain embodiments of my invention for the purpose of illustration, it will be understood generally that adaptations, alterations and modifications thereof occurring to one skilled in the art may be made without departing from the scope of my invention as defined in the appended claims.

T. OKITA.

ALIEN PROPERTY CUSTODIAN

METHOD OF MANUFACTURING RUBBER-LIKE MATERIALS

Tadao Okita, Imazucho, Nishinomiya, Japan;
vested in the Alien Property Custodian

No Drawing. Application filed November 29, 1939

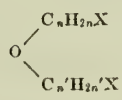
The present application is a continuation in part of my prior copending application Serial No. 94,196, filed August 4, 1936, for "Method of Manufacturing Oil-Proof Rubber-Like Materials".

The present invention relates to a method of manufacturing oil-proof rubber-like materials by the reaction of a dihalogen compound of an olefin such as ethylene or of an ether, a halogen compound of a thio-glycol, or a mixture of the said substances, upon a metallic compound of a thio-diglycol, a metallic compound of glycol, or a mixture of the said substances under ordinary temperature or heating.

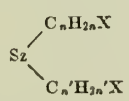
The present invention has for its object an easy manufacture of rubber-like materials of great oil-proof property and elasticity and of the least offensive odor.

Research has heretofore been carried out with a view to improving the quality of rubber which, in spite of its extensive utility, is of very limited oil-proof property and also with a view to developing rubber substitutes of great oil-proof property. Such research has resulted in the manufacture of materials which are not only of as great elasticity as rubber but of great oil-proof property, but these materials have the disadvantages of requiring intricate manufacturing methods and of possessing offensive odors, so that the known processes are still unsatisfactory for practical use.

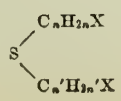
The present invention is the method of manufacturing oil-proof rubber-like materials by the special reaction, under ordinary temperature or heating, of (I) a dihalogen compound of an olefin $C_nH_{2n}X_2$ (e.g. of ethylene), (II) a dihalogen compound of an ether



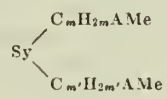
(III) a halogen compound of a polythio-diglycol



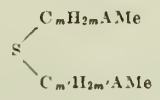
(IV) a halogen compound of a monothio-diglycol



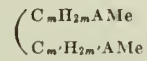
or a mixture of the said substances upon (V) a metallic compound of a polythio-diglycol



(VI) a metallic compound of a monothio-diglycol



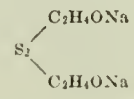
(VII) a metallic compound of a glycol



or a mixture of the said substances. In the above chemical expressions, A is an oxygen group element such as O,S,Se,Te; X is a halogen group element such as Cl,F,I,Br; Me is a metal of the group Na,K,Mg,Ag,Zn,Ca; m,n,m',n',y,z are positive integers; m,m' being between 1 and 2; n,n' being between 1 and 4; y,z being between 2 and 4.

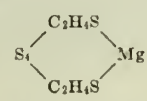
To take a few examples,

(1) The mixture by respective chemical equivalents of (V) di-sulphide of sodium ethylate

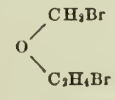


(which is a kind of metallic compound of a polythio-diglycol) and (I) ethylene chloride $C_2H_4Cl_2$ is put in reaction by heating at $70^{\circ}C - 150^{\circ}C$ for about two hours. The ethereal reaction thereby caused separates sodium chloride, leaving a rubber-like material.

(2) The mixture by respective chemical equivalents of (V) a magnesium compound of tetra-thio-di-thio-glycol



(which is a kind of metallic compound of a thio-diglycol) and (II) a bromine compound of methyl-ethyl ether



is put in reaction by heating at $70^{\circ}C - 150^{\circ}C$. The ethereal reaction thereby caused separates magnesium bromide, leaving a rubber-like material.

(3) The mixture by respective chemical equivalents of (VII) potassium glycolate

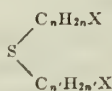


(which is a kind of metallic compound of glycol), and (III) trisulphide of ethyl iodide and propyl iodide

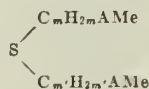


is put in reaction by heating at $70^\circ\text{C} - 150^\circ\text{C}$. The ethereal reaction thereby caused separates potassium iodide, leaving rubber-like materials.

In any case, however, if (I), (II) or (IV) i.e. a dihalogen compound of an olefin or of an ether or a halogen compound of a monothio-diglycol whose chemical expression is



acts upon (VI) a metallic compound of a monothio-diglycol whose chemical expression is



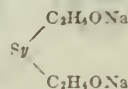
or if (VII) a metallic compound of a glycol acts upon (IV) a halogen compound of a monothio-diglycol; or if (I) or (II) i.e. a dihalogen compound of an olefin or a dihalogen compound of an ether acts upon (VII) a metallic compound of a glycol, not rubber-like materials but a powder is engendered.

It will be clear, therefore, that in reacting (I), (II), (III), (IV) or mixtures thereof with (V), (VI), (VII) or mixtures thereof one should select these compounds or mixtures thereof so as to avoid the above described inoperative combinations (I) + (VI), (II) + (VI), (IV) + (VI), (I) + (VII), (II) + (VII), (IV) + (VII), and so as to give substantially only the following combinations: (I) + (V), (II) + (V), (III) + (V), (IV) + (V), (III) + (VI), (III) + (VII).

Although tests have been conducted on a very large number of reactions typically representative of the various classes of reaction above defined, and although such tests have indicated that nearly all the reactions above defined are effective to produce new and useful compositions most of which have properties resembling those of more or less vulcanized rubber, nevertheless, I believe that the most widely useful new compositions of my invention are those obtained by choosing m , m' , n , n' , y , z , A , Me as follows: m , m' are between 1 and 2 (being preferably 2); n is between 2 and 4; n' is between 2 and 4; y is between 2 and 4; z is between 2 and 4; A = oxygen or sulphur; Me = sodium, potassium or magnesium. (Whenever an integer is defined as be-

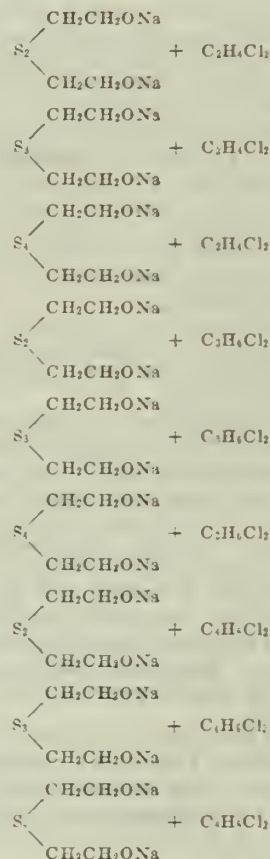
ing between two limiting numbers, the range of values of such integer is to be taken to include both limiting numbers).

In particular I prefer as the very best modes of practising my invention the nine reactions resulting from the combining of (I) + (V) where A = oxygen, X = chlorine, $m = 2$, $m' = 2$, $n = 2$, 3 or 4, and $y = 2$, 3 or 4. These nine embodiments may all be defined as the reactions of a dihalogenated olefin $\text{C}_n\text{H}_{2n}\text{Cl}_2$ (where $n = 2$, 3 or 4) with a polysulphide of sodium ethylate



(where $y = 2$, 3 or 4). The reactions may be effected at ordinary temperatures or at moderately elevated temperatures up to about 150°C .

These nine reactions may be schematically represented as follows:



The materials produced by the present invention have the advantages of great oil-proof property and elasticity, the least offensive odor and an easy method of manufacture.

TADAO OKITA.

ALIEN PROPERTY CUSTODIAN

METHOD FOR THE PRODUCTION OF PRESS MASSES

Franz Nozicka, Vienna, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed December 5, 1939

This invention relates to a method for the production of press masses, and in particular of storage-proof quick or rapid press masses from urea and formaldehyde, and an acid dissociating hardening medium.

When producing press masses from urea-formaldehyde-resins, which masses have to satisfy all modern requirements such as quick press masses, it is necessary that, for the obtention of the very high water stability (boiling proof) and of the rapid hardening speed, besides the suitable condensation method and the correct urea-formaldehyde proportion, sufficient acid is at disposal in the press. Further, it is necessary that the mass for pressing shows at a temperature of 35 to 40° such storing stability that the flowing capability and the other pressing properties are not altered after storing for several months. A press mass corresponding to all requirements must further have the property that, during the pressing operation the acid comes to effect only gradually in order that during the flowing proceeding no hardening of the material takes place, as otherwise, especially when pressing large-size articles, dammings will occur which prevent the perfect pressing. The acid must, however, also not begin to act too late, as otherwise the hardening period is lengthened too much.

To satisfy all these requirements the acid in the press powder must be present in such form, that at temperatures from 35 to 40° no acid is split off, even after storing for months, and that the press powder shows an approximately neutral reaction. During the pressing operation the acid must be liberated only at a temperature which is near to 100°, in order that just sufficient time remains for the uniform outflow and that no damming occurs.

In patent specifications the ammonium salts of weak and strong acids, further the salts of hexamethylenetetramine, of organic bases such as aniline, methylamine, dimethylamine and trimethylamine or ethylamine, diethylamine, and triethylamine, ethanolamine and others are mentioned as substances giving off acid or developing acid. All these compounds have, however, the inconvenience that the salts either undergo strongly hydrolytic dissociation and therefore impart to the press powder a more or less strong acid reaction, or, as all urea-formaldehyde press masses contain small quantities of free formaldehyde or split off them during the storing, opportunity is given that by the formaldehyde the acid is gradually liberated during the storing, as is for instance the case with the ammonium salts,

Other patents intend to obviate these inconveniences by addition of acid anhydrides, such as anhydride of benzoic acid or anhydride of malonic acid and so forth, or esters of various kinds. All these compounds, however, become saponified in the course of time by the small quantities of water contained in any press powder and slowly cause acetification of the press masses. Other patents intend to solve the problem by employment of compounds such as for instance β -hydrobromic cinnamic acid or anhydrides of isodibromic succinic acid.

These compounds give off, however, acid only slowly during the pressing operation or they do not attain the necessary pH.

It has been found that a group of compounds shows all the above mentioned required properties, which group is produced if hexamethylenetetramine is treated with formaldehyde, i. e. 1 mol hexamethylenetetramine with at least 2 mol formaldehyde. In this manner a combination of these two compounds takes place, which is up to the present not yet explained and which represents a quite considerably stronger base than hexamethylenetetramine and the salts of which are only very weakly hydrolytically dissociated. One mol of this compound in n/1 normal solution with $\frac{1}{2}$ mol HCl shows a pH of 6.2. A hexa solution of the same strength, to which $\frac{1}{2}$ mol HCl is added, shows a pH of about 2.

The fatty acid salts of these novel hexamethylenetetramine-formaldehyde compound represent transparent gels, which are clearly soluble in aqueous urea-formaldehyde solutions. For hardening urea-formaldehyde resins gel-like mixed salts of fatty acids and of an other acid such as chloracetic acid, lactic acid or also mineral acid have proved as particularly suitable.

As the formaldehyde is apparently bound only loosely, these salts are always very resistant when care has been taken that no formaldehyde is consumed by any reactions. Only at temperatures near 100° the compound is rapidly dissociated and opportunity is thus given that the whole acid can fully act. Normal urea-formaldehyde condensates have always the tendency to split off small quantities of formaldehyde, and in these the said compounds are therefore very stable. By variation of the mol-proportion hexamethylenetetramine to formaldehyde it is possible, to alter the dissociation temperature of the compound. At about 1 mol hexamethylenetetramine for 3 mol formaldehyde the highest value is attained. Experiments to isolate the hexamethylenetetramine-formaldehyde compound (especially

fatty acid salts) allow to assume that 5 mol hexamethylenetetramine with 12 mol formaldehyde come together to form a monoacid base.

For special purpose the easily isolable, mostly well crystallising double salts of the hexamethylenetetramine-formaldehyde compound, from an acid and heavy metal salts or alkali salts or ammonium salts stood the test. Crystallised double compounds of hexamethylenetetramine-formaldehyde-acids and heavy metal salts have been described by Marcel Delepine C.r. de l'Académie des Sciences 127.622-25.

As suitable condensation methods of urea and formaldehyde or of urea-thio-urea and formaldehyde, all those methods have shown to be suitable, in which that smallest quantity of formaldehyde is employed, which results in a condensation product which does no longer take up further formaldehyde quantities.

Example 1.—One starts for instance from a product which is obtained if urea and formaldehyde in a mol-proportion of 1:1.3 to 1:1.5 at neutral reaction and temperatures of 30 to 40° are condensed during 48 hours. To the condensate which is obtained the gel-like compound of 12 g hexamethylenetetramine, 8 g lauric acid, 0.5 g chloracetic acid and 6 g formaldehyde are added to 360 g urea. Filling substances, such as for instance cellulose, are then worked into the mass which has been obtained, and the mixture is then treated in the usual manner, for instance shaped under heating by pressure. Instead of formaldehyde other aldehydes, aliphatic as well as aromatic, for instance benzaldehyde, can be

brought together with hexamethylenetetramine and acids.

Example 2.—To a urea-formaldehyde condensation product which contains 360 g urea the gel-like mixture from 10 g hexamethylenetetramine and 6 g of palmitic acid, 2 g cetylic alcohol, 0.5 g maleic acid and 20 g cinnamic aldehyde are added as hardening medium, and the mixture thus obtained, which reacts approximately neutral, is kneaded with cellulose and treated in the usual manner to produce press powder. Instead of cinnamic aldehyde the equivalent quantity of benzaldehyde may be used.

The use of toluene-disulfamide resins has also proved to be advantageous, by which addition the flow and the water resisting property are further improved.

Instead of employing ready hexamethylenetetramine the working can be carried out so that by addition of ammonia to the condensate the hexamethylenetetramine is formed in the condensate itself. These compound types may be employed with great advantage also for the production of castings from urea-formaldehyde resins, as by keeping correctly increased drying temperatures it is possible to carry through the dehydration of the cast articles without hardening and to make the final acid hardening take place only at increased temperature.

Also hot varnishes of urea-formaldehyde resins give excellently brilliant elastic films when these compounds are used as hardening medium.

FRANZ NOZICKA.

ALIEN PROPERTY CUSTODIAN

FILM-FORMING COMPOSITION AND PROCESS FOR PREPARING THE SAME

Fritz Jage, Saarau Kreis Schweidnitz, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed December 14, 1939

The present invention relates to a film-forming material and a process for preparing the same, and it has particular relation to the production of such material from sulfur-containing condensation products of high-molecular weight.

A further object of my invention is the use of said film-forming material for the preparation of coatings, impregnations, cementing layers, or the like.

It is known that highly polymerized, rubber-like condensation products, which contain sulfur, can be obtained by causing a reaction of an inorganic water-soluble polysulfide with an organic compound containing replaceable negative groups, such as dihalogenated paraffin hydrocarbons. By carrying out this reaction in an aqueous medium in the presence of an inorganic dispersing agent, such as magnesium hydroxide, and, if desired, with the simultaneous use of an organic protective colloid substance, the condensation product is obtained in the form of a finely divided latex-like suspension in water. This finely divided product is washed with water, coagulated with acid, and, by a treatment on rolls, is converted into rubber-like sheets which are used for the production of soft rubber-like articles.

It is also known that the condensation products thus obtained show an extraordinary resistance to organic solvents. They neither dissolve nor swell in most of the organic liquids and they have found numerous applications owing to their stability when in contact with solvents. A general application of these products was, however, prevented hitherto precisely because of their stability to such solvents, as the production of articles from these products was limited to the use and working of the solid material obtained by coagulation. It was not possible to use said condensation products for the production of coatings or impregnations in the form of solutions, or as pastes or cements capable of being spread.

The above mentioned aqueous, latex-like suspensions of the sulfur-containing condensation products can not be used for the production of coatings or the like, as such suspensions do not yield coherent coatings or films when dried at ordinary or elevated temperatures. By drying such suspensions, cracked, non-coherent products of poor adhesive power are obtained, which are neither sufficiently waterproof, nor resistant to acids or free from pores.

I have found that a suspension of the above mentioned sulfur-containing condensation products, which forms a coherent, homogeneous film

on drying, and can be used as a valuable coating, impregnating or adhesive composition, can be prepared by proceeding as follows:

An aqueous suspension of a sulfur containing, organic condensation product of the above mentioned class, which contains magnesium hydroxide as a dispersing agent, is treated with an ammonium salt or an aqueous solution of the same. I have found that ammonium salts cause solution of magnesium hydroxide without causing coagulation of the suspension. The dissolved magnesium hydroxide can be removed from the latex-like dispersion by decanting it with water.

Example 1.—An aqueous suspension is prepared in a known manner from the condensation product of ethylene chloride and sodium tetrasulfide in the presence of magnesium hydroxide as a dispersing agent. Such a condensation product of ethylene chloride and sodium tetrasulfide is, for example, obtained by the condensation of 460 parts by weight of ethylene chloride and 3980 parts by weight of an aqueous solution containing 860 parts by weight of sodium tetrasulfide. Condensation is carried out in the presence of 15 parts by weight of freshly precipitated magnesium hydroxide. The suspension obtained in a known manner has a dry content of about 7%, and about 2% ashes, calculated on the dry content. 1200 grams of this suspension are mixed with 30 grams of ammonium sulphate and stirred at about 30°C for about 2 hours. The suspension is then allowed to settle; the liquid, which remains above the condensation product, is removed, and the condensation product is washed by decanting it twice with 1000 cc. water each time. The latex-like dispersion thus obtained shows the above-mentioned film-forming capability. This dispersion can be used for preparing coatings, impregnations or adhesive layers, and yields on drying valuable, coherent, homogeneous and highly resistant films or the like which contain only about .4% ashes.

Example 2.—1200 grams of the aqueous suspension prepared as described in Example 1, are mixed with 20 grams of ammonium oxalate and stirred at about 30°C for about 2 hours. The suspension is then allowed to settle. The liquid which remains above the condensation product, is removed, and the condensation product is washed by decanting it twice with 1000 cc. water each time.

Example 3.—1200 grams of the aqueous suspension prepared as described in Example 1, are treated with 10 grams of ammonium chloride at about 70°C for about 2 hours. The fur-

ther treatment is carried out as described in Example 1. A latex-like dispersion is obtained which forms a coherent, homogeneous film free from cracks.

Example 4.—1000 grams of an aqueous suspension of the type described in Example 1, having a dry-content of about 10%, is treated with 240 grams of an aqueous solution containing about 16% ammonium nitrate under stirring at about 30°C for about 2 hours. The further treatment is carried out as described in Example 1. A latex-like dispersion is obtained which shows valuable film-forming properties.

In carrying out my present invention any ammonium salt of an inorganic or organic acid can be used which is capable of causing solution of magnesium hydroxide in water. The dispersion of the organic polysulfide to be treated may have a lower or higher dry content, and the treatment with ammonium salts can be carried out at ordinary or elevated temperatures for a longer or shorter period. The amount of the ammonium salt to be used depends on the specific salt, on the dry content of the suspension to be treated, and the temperature and duration of the treatment. The ammonium salt should, of course, be used in an amount which essentially effects dissolution of magnesium hydroxide under the working conditions used. This amount can easily be determined by preliminary tests. The term "ammonium salt" as used in the present specification and claims denotes any ammonium salt which is capable of causing dissolution of magnesium hydroxide in water. The treatment of the suspension with ammonium salts can be carried out in several steps, whereby the ash-content of the suspension is further reduced by each step. Thus a suspension can be obtained the ash content of which amounts to less than 0.1 to 0.2% calculated on the dry content of the suspension. Mixtures of several ammonium salts may also be used. My invention can be carried out with any highly polymerized sulfur-containing condensation product obtained in the presence of magnesium hydroxide as a dispersing agent. Instead of ethylene chloride, other organic compounds, which are capable of reacting with inorganic polysulfides at least at two link-

ages, can be employed. Suitable organic compounds are, for example, dihalogenated hydrocarbons, dihalogenated ethers, esters and acetals, alkyl dithiosulfuric acids, such as ethyl dithiosulfuric acids, alkyl dimercaptans, such as ethyl dimercaptans. Mixtures of several organic compounds may also be used.

The products obtained from the material prepared according to my present invention, show valuable chemical and physical properties. They have an ash-content of only 0.2 to 0.5%, are highly impermeable to water and to aqueous solutions of acids, such as concentrated hydrochloric acid. They also show an extraordinary resistance to organic substances, and are not affected by dissolution or swelling when subjected to the action of aliphatic and aromatic hydrocarbons, motor fuel, solvents, oils etc. They possess a high resistance to aging and atmospheric influences, and are inert to ozone. Thus, the products obtained according to my invention show essentially the same valuable properties as the plastic products obtained from aqueous suspensions of the sulfur-containing, organic condensation products by coagulating said suspensions with an acid.

By the process of my invention latex-like suspensions can be obtained which yield coatings, impregnations, cementing layers, or the like, having the above mentioned valuable properties. The suspensions can be used without any admixture. They can also be used with the addition of other materials, such as fillers, pigments, vulcanizing agents, etc., as I have found that the addition of fillers or the like to the suspensions prepared according to my present invention, does not injuriously affect the film-forming properties. Furthermore, the suspensions can be subjected to a solidifying heat treatment with or without the addition of other substances, in a similar manner to that already known in the treatment of highly polymerized, rubber-like sulfur-containing condensation products. Such heat treatment is, for example, described in the U. S. Patent No. Re. 19,207 to Patrick, page 2, lines 61-64.

FRITZ JAGE.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF ALICYCLIC ALCOHOLS

Willi Schmidt and Karl Seydel, Ludwigshafen-on-Rhine, and Hugo Kroeper, Heidelberg, Germany; vested in the Alien Property Custodian

No Drawing. Application filed December 14, 1939

This invention relates to the production of alicyclic alcohols; and more particularly it concerns the production of such alcohols from cyclic nitrogenous compounds containing six-membered carboxylic rings and one nitrogen atom, the rings being free from substituents other than those containing exclusively carbon and hydrogen atoms.

Cyclohexanol and its homologues and analogues in general are extremely valuable as solvents and as starting materials in organic processes. Methods already are known for the production of such alcohols involving the hydrogenation of phenols in the presence of catalysts.

The present invention is based upon the discovery that alicyclic alcohols may be prepared in highly satisfactory yields in a simple manner from starting materials different from phenols. By heating a compound of the type described above, for example cyclohexylamine, methylcyclohexylamine, dicyclohexylamine, decahydronaphthylamine, or mixtures thereof with hydrogen and a hydroxyl-containing compound, such as water or an alcohol, in the presence of a hydrogenation catalyst, alicyclic alcohols are formed together with ammonia or ammonia substituted by the radicle of the hydroxyl-containing compound.

In its broadest scope the invention involves heating cyclohexylamine or its homologues or analogues or any compound capable of being converted into or capable of yielding cyclohexylamine or its homologues or analogues with hydrogen and a hydroxyl-containing compound in the presence of a hydrogenation catalyst.

As catalyst there may be used in particular the metals of the 8th group of the Periodic Table, in particular the non-noble metals, or copper metal or oxydic or sulfidic hydrogenation catalysts. The preparation and the composition of these catalysts has extensively been studied and described in connection with the catalytic hydrogenation of aniline to form cyclohexylamine, with the production of alcohols from fatty acids or with the conversion of carboxylic acids, ammonia and hydrogen into amines or with the production of amines from carboxylic acid nitriles. These catalysts may be employed either alone or applied to the conventional carrier substances, such as pumice stone, aluminium oxide, fused silica gel and the like. It will be understood that the above given explanation of the catalysts is merely given for purposes of illustration and that the specific catalyst is not an essential part of our invention but that numerous modifica-

tions of these catalysts may be made without departure from the spirit of our invention and that any other of the catalysts employed in hydrogenations of the type referred to above may be used.

The reaction according to our invention is preferably carried out under energetic conditions. The catalysts should be employed in a highly active state and the process is conducted preferably at temperatures ranging from 160 to 400°C, and in particular from 180° to 330°C. When working in the vapor phase, it is particularly suitable to work at temperatures below 250°C; the liquid phase process is preferably conducted at temperatures exceeding 220°C. A substantial excess of the hydroxyl-containing compound over that required to substitute a hydroxyl group for a nitrogenous group, e. g. the amino group, for example from 2 to 50 times, should be employed. Suitable hydroxyl-containing compounds are in particular water, and also low molecular aliphatic alcohols, such as methanol, ethyl, propyl or butyl alcohol and the like. It is self understood that higher alcohols may also be used but this does not involve economic advantages because too large a radicle attached to the hydroxyl group simply constitutes a diluent decreasing the yield per unit of time and reaction space and slowing up the process.

The reaction may be carried out in the liquid phase or in the gas phase. It is possible to employ inert solvents for the reactants or inert diluent gases when working in the gas phase. By working under superatmospheric pressure it is possible to maintain a high hydrogen concentration even when working with a considerable excess of the hydroxyl-containing compound. The pressure, when employed, may be within the range of from 10 to 250 atmospheres, but higher pressures, such as 300, 400, 500 or more may be employed.

The process may be conducted continuously for example by leading a vaporious mixture of cyclohexylamine, steam and hydrogen through a tube or a plurality of tubes charged with a hydrogenation catalyst. When working continuously in the liquid phase, the liquid mixture of cyclohexylamine and water or alcohol may be pressed through a vessel wherein the catalyst may be rigidly arranged, while at the same time leading hydrogen in the same direction in a cycle through the vessel. The liquid starting material may also be allowed to trickle over the catalyst while leading in hydrogen in counter-current together with

a vaporized hydroxyl-containing compound of the kind defined above.

The actual temperature to be used depends on the activity of the catalyst and on the time of contact between the reaction mixture and the catalyst. In general, the time of contact should be long enough to ensure that the starting material introduced is at least partly subjected to cyclohexanol formation before leaving the catalyst. However, the temperature should not be so high and the time of contact should not be so long as to favor substantially the formation of aromatic or alicyclic hydrocarbons which may occur under too energetic conditions.

A preferred embodiment of our invention consists in using as starting materials nitrogenous aromatic compounds which are capable of being converted under reaction conditions into cyclohexylamine or its homologues and analogues as defined above. Suitable compounds of this type are, for example, aniline, naphthylamine, diphenylamine or their alkyl substitution products, e. g. toluidines or phenylcyclohexylamine or even nitrobenzene, nitrosobenzene, phenylhydroxylamine, the nitrogenous group of which is easily converted into an amino group during or before the hydrogenation of the benzene nucleus.

Generally speaking, the reaction conditions for converting one of the aromatic nitrogenous compounds of the kind referred to above into alicyclic alcohols are similar to those used in the production of alicyclic alcohols from alicyclic amines. A substantial excess of the hydroxyl-containing substance should be employed. In selecting the hydrogenation catalyst care should be taken that the benzene nuclei are hydrogenated. Metals of the 8th group of the Periodic Table are particularly satisfactory in this respect. The reaction conditions should be chosen accordingly; in particular, the reaction is preferably carried out under increased pressure and at temperatures exceeding 250° C, if nitrohydrocarbons are the starting materials.

The following Examples serve to illustrate various modifications of our invention. It is, however, not restricted to these Examples. The parts are by weight unless otherwise stated.

Example 1

100 parts of nickel carbonate are intimately mixed with 4 parts of chromic acid anhydride and the whole then reduced in a stream of hydrogen.

10 parts of cyclohexylamine, 10 parts of water and 1 part of the catalyst are charged into a stirring autoclave and heated at 300°C with hydrogen under a pressure of 250 atmospheres for some hours. The reaction mass is allowed to cool, filtered off from the catalyst and admixed with sulphuric acid in order to eliminate the basic compounds. The cyclohexanol is then purified by distillation. 5 parts of cyclohexanol are thus obtained corresponding to a yield of 90 per cent calculated on the amount of cyclohexylamine converted.

When starting from 10 parts of dicyclohexylamine or of a mixture of equal amounts of cyclohexylamine and dicyclohexylamine, cyclohexanol is formed under otherwise identical conditions in a 93 per cent yield. Good yields are also obtained when lowering the reaction temperature to 250°C, the time of the reaction being somewhat longer.

Example 2

A mixture of 10 parts of aniline, 30 parts of methanol and 1 part of a copper catalyst applied to silica gel (copper content 20 per cent; chromic oxide content 0.9 per cent) are filled into a stirring autoclave. Hydrogen is then pressed in at room temperature under a pressure of 30 atmospheres. The whole is then heated to 300°C, whereby the pressure reaches 276 atmospheres. The reaction mixture is allowed to cool and the pressure is released. A mixture of hydrogen and methylamine escapes. The reaction mixture is filtered off and worked up in the manner described in Example 1. Cyclohexanol is thus obtained in a yield of 82 per cent.

Example 3

100 parts of cobalt carbonate are intimately mixed with 4 parts of chromic acid anhydride and the whole is reduced in a stream of hydrogen. 10 parts of aniline, 10 parts of water and 1 part of the catalyst are heated in a stirring autoclave to 300°C, while simultaneously pressing in hydrogen under a pressure of 250 atmospheres. During the reaction the hydrogen pressure is partly released three times in order to remove as far as possible the ammonia formed. After hydrogen is no longer absorbed, the reaction mixture is allowed to cool and filtered off from the catalyst. The oily layer of the filtrate is subjected to an azeotropic distillation with benzene in order to remove water. The cyclohexanol remaining back is purified by fractional distillation. The aminic bodies mostly mono- and dicyclohexylamine, obtained as by-products are again used for the production of cyclohexanol. The yield is 6.5 parts of cyclohexanol.

Example 4

20 parts of nickel oxide, 6 parts of copper oxide and 1 part of chromic oxide are precipitated on 7.3 parts of pumice stone. The catalyst is then reduced.

Over this catalyst there is led per hour 90 times its volume of hydrogen admixed with 3.5 per cent per volume of vaporous aniline and 25 per cent per volume of steam. The mixture emerging from the catalyst is condensed. From the condensate the ammonia dissolved therein is removed by gently heating and from the hydrogen the ammonia is also removed.

The ammonia-free condensate is vaporized in a stream of ammonia-free hydrogen and led over a catalyst of the above described composition under the same conditions. This process is repeated twice. The condensate obtained by cooling the reaction mixture emerging from the fourth catalyst is practically free from amines. The aqueous part of the condensate is given back into the mixture to be led over the first catalyst. The yield of crude cyclohexanol is 102 parts for 100 parts of aniline.

Example 5

Over 100 liters of a nickel catalyst activated by chromium, zinc and barium applied to pumice stone (the catalyst contains per 100 parts of nickel 2 parts of chromium oxide, 1.5 parts of zinc oxide and 2 parts of barium oxide) there is led per hour at from 180 to 190 C a mixture of 8,000 liters of hydrogen, 1,500 grams of vaporized aniline and 6,000 grams of steam. The gas mixture emerging from the catalyst is suitably condensed whereby two condensates are obtained, the first consisting of crude cyclohexanol and the second

of water free from ammonia. The residual gas consisting of hydrogen and ammonia is freed from ammonia. The hydrogen is again mixed with vaporous aniline and steam and thus again used for the reaction.

The crude cyclohexanol which contains small amounts of cyclohexanone is led together with hydrogen under 200 atmospheres pressure in the same direction over a nickel catalyst as described in Example 4 contained in a vertically arranged tower. The product thus obtained is separated by a fractional distillation into cyclohexanol and into amines which are given back into the first stage of the process. The yield of cyclohexanol amounts to from 94 to 96 per cent of the theoretical yield.

Example 6

12.3 parts of nitrobenzene, 10 parts of water and 1 part of the catalyst described in Example 1 are treated at 300°C with hydrogen under a pressure of 250 atmospheres for 6 hours. The reaction product is filtered off from the catalyst and then subjected to a fractional distillation. Cyclohexanol is thus obtained in a yield of 94 per cent of the theoretical yield.

Example 7

15. parts of para-toluidine, 10 parts of water and 1 part of the catalyst described in Example 1 are heated in a stirring autoclave to from 260° to 280° C while simultaneously pressing in hydrogen under 250 atmospheres pressure. During the reaction the pressure is released twice to 150 atmospheres.

The reaction mixture is worked up in the manner described in Example 1, whereby para-methylcyclonexanol is obtained in a yield of 91 per cent.

Example 8

10 parts of decahydronaphthylamine, 10 parts of water and 1 part of the catalyst described in Example 1 are heated in a stirring autoclave to from 280° to 300° C while continuously maintaining a hydrogen pressure of 250 atmospheres. The pressure is released three times down to 100 atmospheres. Decahydronaphthol is thus obtained in a 90 per cent yield.

WILLI SCHMIDT.
KARL SEYDEL.
HUGO KROEPER.

ALIEN PROPERTY CUSTODIAN

METHOD AND APPARATUS FOR PRODUCING LINEAR POLYMERS

Alfred Friederich, Berlin-Wilmersdorf, and Paul
Schlack, Berlin-Treptow, Germany; vested in
the Alien Property Custodian

Application filed December 15, 1939

This invention relates to the production of synthetic linear polymers.

In the production of linear fusible condensation polymers, especially polyamides, such as condensation products of ω -aminocarboxylic acids with 5 or more chain-members between the amino- and the carboxylic acid groups, of condensation products from $\alpha\omega$ -diamines and $\alpha\omega$ -dicarboxylic acids or functional derivatives thereof, or of polymerizates of lactams according to the U. S. Patent Application Ser. No. 220,266 filed July 20, 1938, it has proved advantageous, to work under pressure in the first step and then to finish off the reaction at reduced pressure, for instance at atmospheric pressure and in vacuo. The greater pressure in the first step accelerates the reaction, since the formation of the polymers is followed by a contraction in volume. In the second step with lower pressure or with sub-atmospheric pressure the volatile reaction products, solvents or unreacted starting materials (monomers) and volatile accelerators are intended to be removed. Treatment under pressure during the first step is especially advantageous if it is desired to accelerate the reaction, for instance the polymerization of a lactam by volatile compounds capable of being acylated, such as alcohols, water, ammonia, amines. In this case already a comparatively small amount, for instance 1/60 to 1/6 mol of these compounds calculated on 1 mol lactam causes the time of reaction to be substantially shortened as against the time required by working at atmospheric pressure.

It is an object of this invention to provide a continuous process of producing linear synthetic polymers.

A further object of the invention consists in the provision of suitable apparatus' by which the process can be carried into effect.

Still further objects reside in details of the construction of the said apparatus as will be more fully understood with reference to the accompanying drawing.

Figure 1 is a diagrammatic cross sectional view of an apparatus suitable for the continuous production of linear superpolymers.

Before dealing specifically with the single Figure it appears necessary to explain the principle of the invention.

We have found that the production of polyamides can be carried out with great advantage continuously even under conditions which necessitate the removal of volatile by-products by feeding the liquid or liquified starting material by means of suitable feeding means in practically uniform amount calculated on the end products continuously in several different pressure steps through the apparatus wherein each step of high pressure is followed by a step of lower pressure.

The reaction mixture may contain all necessary additions before it is fed to the apparatus. A process of this kind in which any desired number of double steps may be employed has proved especially valuable if during the reaction substantial amounts of volatile compounds, for instance water or alcohol must be added in order to accelerate the reaction. And furthermore if compounds are added during the reaction which improve the products or which form interpolymeric modifications with these compounds, reacting with a renewed formation of volatile compounds, or if substantial amounts of volatile compounds are gradually set free during the polyamide-formation, for instance if acids are split off from esters, alcohols, phenols or acyl compounds.

Organic polymers of the kind described especially fusible polyamides serve very often for the production of shaped articles of uniform diameter which are formed either in the plastic or fused state by extrusion from a mouth piece or from the openings of, for instance a spinneret. In the first case the production of rods or tubes of all kinds, in the second case the production of threads, bristles, horse-hair etc. is concerned. Hitherto it has been usual to solidify the final product of the polymerization from the melt in the form of rods, blocks, ribbons etc. or to lead the same from openings into water whereby cable or ribbon-like irregular articles are obtained. These products were then again melted at a suitable temperature and pressed through openings in the manner described above.

We have found further, that the above described process for the production of the polymerizate may be combined with great advantage with the known process for the production of shaped articles from the melt. According to the invention the throughput through the polymerization apparatus is so adjusted that the amount of material which is subjected to treatment, i. e. including any additions made during the reaction, corresponds at all times with the amount of material which is mechanically shaped. In this manner the amount of polymerizate which is continuously produced leaves the apparatus after it has been mechanically shaped without any interruption of the process. It is evident that this last step which no longer effects any chemical change but is subject only to the laws of physics will usually require other conditions of pressure and temperature as the preceding steps of polymerization or condensation. According to this invention therefore the process is further so developed that polymerization or condensation and the shaping are carried out under different conditions of pressure and temperature adjustable at will.

Since uniform pressure does not prevail in

the different steps of the process, the pressure rising and falling all the time, it is of course necessary to provide several pumps for increasing the pressure, for instance worm pumps or gear pumps which feed the material under treatment on after the pressure has been released, under the pressure prevailing in the next step. A suitable apparatus for carrying the process into effect is shown diagrammatically in the single Figure of the drawing. Each double step of the polymerization apparatus consists of two containers in different pressure which are mounted one after the other. Two of such steps are shown in the drawing, they can, however, if necessary, be increased in number. A feeding pump is arranged between the container of lower pressure b_0 , b_1 , b_2 and the subsequent containers of higher pressure a_1 , a_2 , a_3 . The feeding pump may be a gear pump c_0 , c_1 , c_2 , the sucking side of the pump being connected with the container of lower pressure, the pressing side with the subsequent container of higher pressure. This pump does not only separate the two containers but also adjusts the pressure prevailing in any of the containers. The container of higher pressure is advantageously arranged as a heating pipe system with pipes g_1 , g_2 , g_3 which are surrounded by a heating liquid from without. The heating pipe system and the expansion vessel are separated by throttle valves d_1 , d_2 by means of which the surplus pressure in the heating pipe system is adjusted.

The amount of material used up during the continuous process must be continuously substituted. A float chamber b_0 the content of which is continuously refilled from a container, serves this purpose. The refilling is controlled by the float valve v . From this float chamber the first pump c_0 feeds the liquid starting material, for instance ϵ -caprolactam with a certain water content and with a content of substances which control the polymerization such as ϵ -aminocaproic acid hydrochloride before polymerization. The material is fed under pressure into the first heating pipe container a_1 . The partly polymerized material is fed to the sucking side of pump c_1 after it has been led through the throttle valve d_1 into the vessel b_1 where the pressure is released. The material leaves pump c_1 again under high pressure. It is led into the heating pipe system a_2 for its second polymerization step and this is repeated as often as is necessary under the special conditions of the polymerization.

Of course, it cannot be expected that all pumps c_1 , c_2 , c_3 which work under different conditions of temperature and pressure feed exactly the same amount of material even if they are of even size and run the same revolutions per minute. According to the invention the pumps at the beginning of the working step are given a certain overfeed and a bypass tube e_0 , e_1 is arranged which leads from the pressure side to the sucking side of the pump and which incorporates a throttle valve f_0 , f_1 . In this manner an adjustment of the throttle valves enable the amount fed by the previous pump to be brought into an agreement with the amount fed by the subsequent pump. The inspection glasses m_0 , m_1 on the containers b_0 , b_1 aid in controlling the surface of the liquid in the containers and enable the surface to be kept constantly on the same level. For the polymerization preferably heating pipe systems a_1 , a_2 , a_3 are employed, the material under treatment following slowly through the tubes g_1 , g_2 , g_3 . Since the speed of flow in these tubes is com-

paratively small, owing to the long time of polymerization, there is a certain danger of the individual tubes being unevenly flown through. Each heating pipe system is therefore closed on its entrance side by a perforated nozzle plate i_1 , i_2 , i_3 through which the entering material has to pass. The resistance of the narrow orifices of this perforated plate is so selected that the resistance of flow of the tubes can be neglected. In this manner the same amount of liquid per time unit flows through each of the tubes. The perforated nozzle plate may also be arranged at the exit side, where it may simultaneously act to stow the pressure in the tubes. Under certain circumstances they may substitute the throttle valves d_1 , d_2 . As a rule, however, it is more advantageous to employ the perforated plate only for the division of each pressure step. If the perforated plate is mounted in the upper end of the heating pipe system it is sometimes necessary to provide an outlet from the upper end to the vessels b_1 , b_2 by means of a special pipe.

If the material is to be formed without intermediate solidification immediately following the polymerization an apparatus is employed which is connected to the last container of the polymerization reaction without any intermediate tubings etc. In this case one of the known devices for the production of pressure, for instance a gear pump, is employed furthermore a heat exchange system in order to exactly control the temperatures necessary for shaping, a filtering arrangement, for instance the metal screen k and immediately connected therewith a die mould for the production of profiled rods, tubes etc. or a spinneret or a number of spinnerets arranged in parallel position for the spinning of fibers, monofilaments, bristles, horse-hair etc. All these parts are mounted together as narrowly as possible to form a single complete apparatus without any pipe line connections, in order to provide the shortest route from the end from the final phase of the polymerization of the spinnable melt to the mouth piece l of the shaping device.

If it is desired to change the throughput per time unit corresponding with different diameters or different shaping speeds at the exit of mouth piece l , the amount fed by the different pumps c_1 , c_2 , c_3 is made to correspond with the changing speed by changing the amount of revolutions of the pumps per minute, if the chemical reaction, as in the case of the polymerization of ϵ -caprolactam in the presence of an agent controlling the polymerization such as ϵ -aminocaproic acid hydrochloride, permits. This measure is also selected if a change in the duration of the polymerization is necessary owing to the changing conditions of the chemical reaction.

The process which is carried out in different vessels and pipe systems under varying pressures also necessitates different reaction temperatures. In order to provide for these varying temperatures a number of heating zones, for instance circuits 1 to 6 are arranged which can partly be interconnected. It is not difficult to keep the temperature of the heating agent in these circuits at an even level. In this manner it is possible to graduate the reaction and working temperatures in the different vessels a_1 , a_2 and b_1 , b_2 according to the necessities of the chemical or physical process.

The introduction of additional reaction components is carried out after the first pressure heating, if several double steps are employed advantageously after the first double step before the

pressure pump which in this case acts at the same time as a pump and as a homogenizer. Naturally additional homogenizing devices may be installed.

If larger amounts of volatile products are formed during the reaction or if volatile products, for instance water or alcohol are added in larger amounts from the start it may be of advantage to employ a horizontal tube in the pressure phase, the cross section of which is only partly filled up by the flowing mass. The surface in which the melt and the vapors contact may be enlarged by arranging walls which may be disposed one from the top and one from the bottom or by moving parts, for instance flat feeding worms.

The following examples illustrate the invention:

Example 1

The mixture of 100 parts of ϵ -caprolactam, 0.75 parts of ϵ -aminocaproic acid hydrochloride and 4 parts of water are pressed through a heating apparatus as described in the drawing. The apparatus being so arranged that the mass is left for 4 hours in the first heating zone, kept at 220° C, then flows through the first pressure release vessel heated to 230° C in the course of 2 hours.

On its way to the second pressure heating system 5 parts of 9-aminononanoic methylester are added to the melt in order to improve the stability of the final product and the mixture is homogenized by the pressure pump. The mixture flows through the second pressure phase in 2 hours at 240 to 250° C and is then kept in the second pressure release vessel for 1 hour at 250° C in order to remove the alcohol formed. From there it flows continuously on to the heat exchange system which feeds the melt to the spinneret at a temperature of 230° C.

Example 2

A mixture of 113 parts of ϵ -caprolactam, 0.2 parts of ethyl alcohol, 0.6 parts of ϵ -aminocaproic acid chloride is pressed in the course of 1.5 hours at 230° C through the first pressure phase of the apparatus illustrated in the drawing. Upon leaving the heating pipe system the pressure in the mass is released and the mass flows at atmospheric pressure through a slightly inclined tube heated to 240° C in the course of 2 hours, in which time the alcohol distills off. After the mass has left the intermediate vessel 20 parts of molten 9-formylaminononanoic acid are introduced therein by means of a gear pump and the mass is homogenized for the second pressure phase by the pressure pump. The melt is pressed through the second pressure phase in an hour at a temperature of 240 to 250° C and reaches a second horizontal vessel kept at a vacuum of 10 mm. The mass flows through this vessel in 2 hours at a temperature of 240 to 250° C. The newly formed volatile components have been distilled off in the second reduced pressure phase. The mass is pressed by means of a gear pump through a heat exchange system having a temperature of 230° C and from there to a series of 5 spinnerets arranged in parallel each having 16 holes of 0.4 mm diameter. The threads leaving the spinnerets are drawn off with a speed of 250 meters per minute. By cold drawing the threads a tensile strength of 4 to 5 grams pro deniers is obtained.

Example 3

A mixture of 100 parts of ϵ -caprolactam and 10 parts of water flows through the first pressure phase

with a temperature of 230° C in 40 minutes. The pressure is released in the first low pressure phase and the mass is pressed after remaining at atmospheric pressure for 1 hour into a second high pressure phase at a temperature of 255° C. After 2 hours the melt reaches the second horizontal low pressure vessel and passes therethrough in a relatively thin layer of about 4 cm height in 2 hours at a temperature of 250° C. On its way to the spinneret the temperature is finally adjusted at 230° C.

Example 4

ϵ -aminocaproic acid ethylester is pressed in 2 hours through the first pressure phase at 220° C. After the pressure has been released to atmospheric pressure the precondensed mass flows through a horizontal tube at 230° C in 2 hours, the splitting off of alcohol being continued. In the subsequent high pressure phase which is again passed through in 2 hours, the temperature is increased to 250 to 265° C. The pressure is now released and the mass introduced into a flat horizontal tube-shaped vessel maintained under a vacuum of 2 mm Hg. During this stage the ϵ -caprolactam formed as a by-product is separated in vapor form. After being kept in the low pressure phase for 2 hours the polyamide melt is shaped into a continuous rod of 8 mm thickness by means of a spinneret.

Example 5

A mixture of 8 parts of ϵ -caprolactam and 2 parts of 9-aminononanoic acid is pressed inside half an hour through a heating pipe system kept at 210° C and arranged vertically, then fed into a flat tube-shaped vessel, heated to 230° C, the surplus pressure being released. After remaining in the pressureless phase for 3 hours the mass enters a second high pressure heating system kept at 250° C, flows therethrough inside 2 hours and reaches another horizontal tube-shaped vessel evacuated for the purpose of removing volatile components (monomers), the vessel being kept at 250° C and being passed by the melt in 1.5 hours before the melt is shaped by means of a spinneret.

Example 6

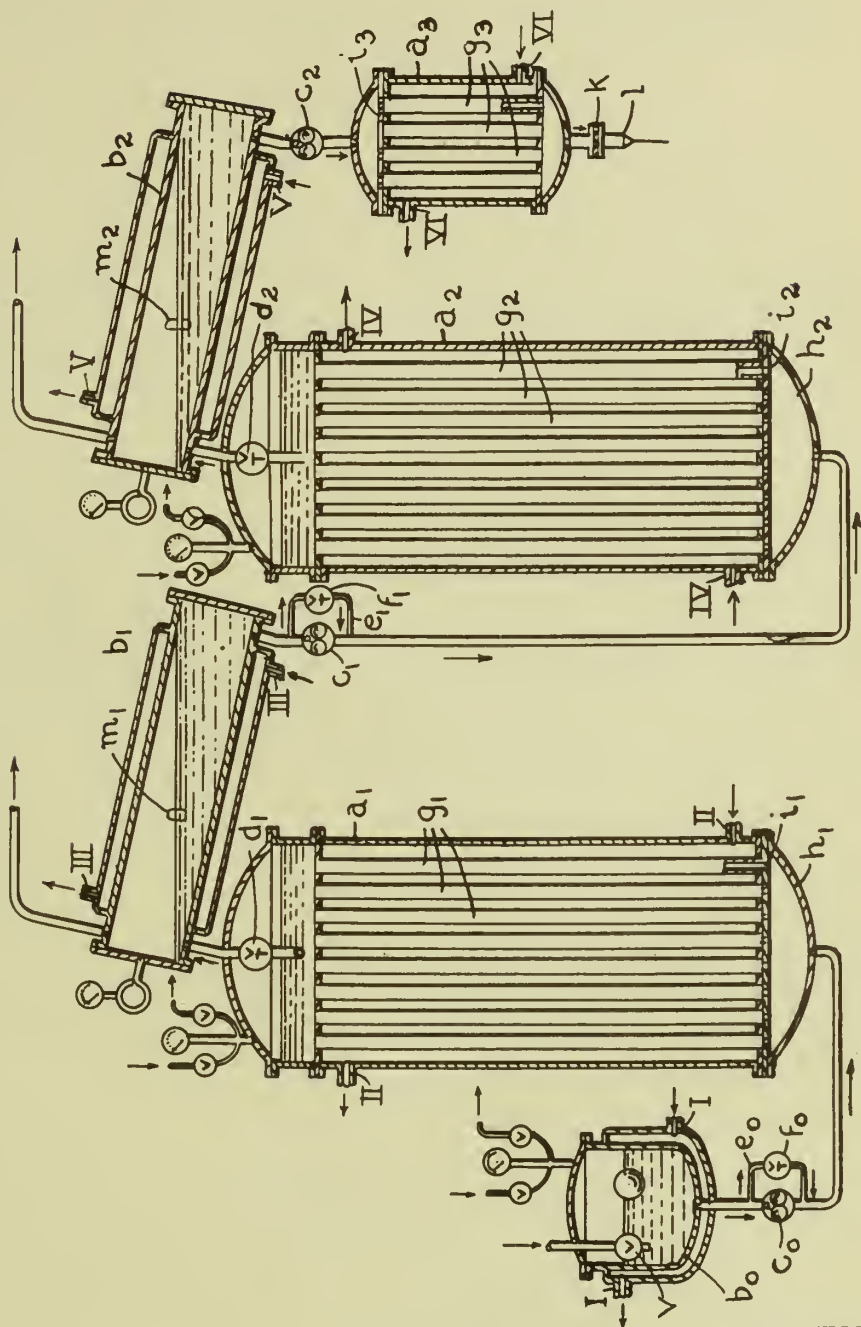
A mixture of 108 parts of adiponitrile, 116 parts of hexamethylenediamine and 50 parts of water containing $\frac{1}{16}$ of the amount of hydrogen sulfide necessary for neutralizing the diamine, is led in 5 hours through a flat horizontal pressure tube in which the temperature rises gradually from 200 to 270° C. At the end of the tube ammonia, hydrogen sulfide and steam and the molten polyamide are continuously removed by separate members, the pressure being released to atmospheric. The melt is fed into a second horizontal tube heated to 275° C. After remaining therein for an hour the melt is pressed into a horizontal heating pipe system kept at 280° C. After flowing therethrough for 2 hours the mass again reaches a flat tube-shaped vessel in which it is freed of the remaining volatile compounds in the course of 1.5 hours at 260 to 280° C at a pressure of 2 mm. The finished polyamide is finally continuously pressed through a slot into cold water.

ALFRED FRIEDERICH.
PAUL SCHLACK.

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A. FRIEDERICH ET AL
METHOD AND APPARATUS FOR PRODUCING
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INVENTORS
Alfred Friederich
Paul Schlack
BY *R. F. Miller*

ATTORNEY



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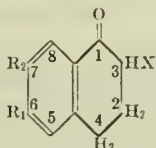
ANALGETICALLY EFFECTIVE TETRAHY- DRONAPHTALENE DERIVATIVES

Georg Scheuing and Bruno Walach, Ingelheim
A. Rh., Germany; vested in the Alien Property
Custodian

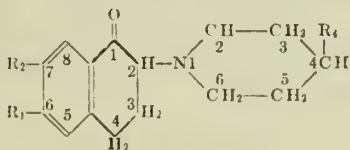
No Drawing. Application filed December 16, 1939

This invention relates to new analgetically effective tetrahydronaphtalene derivatives and to processes for their production.

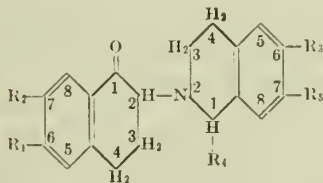
According to the invention the production of the new compounds takes place in such a manner, that 1-oxo-2-halogen compounds of the tetrahydronaphtalene of the general formula



in which X means one halogen atom are converted in 2-position with a hydrogenated heterocyclic nitrogen base, such as piperidine, tetrahydroisoquinoline or derivatives of these compounds according to known methods to the new compounds which have the general formula



or



In these formulae mean R_1 and R_2 hydrogen atoms, oxy-, alkyloxy- or alkyl groups and R_3 , R_4 and R_5 hydrogen atoms, alkyl- or alkyloxy groups.

The production of the new compounds can take place for instance in that 1-oxo-2-halogen tetrahydronaphtalene is converted in presence of organic solvents with the hydrogenated base, filtered off from the halogen hydrate produced as by-product, and the amino ketone contained in the organic solvent and formed in the conversion is extracted by diluted acids.

For 1 mol of β -halogen- α -tetralon preferably at least 2 mol of nitrogen base are used, as at the conversion 1 mol of halogen hydrogen is formed, which is bound by 1 mol base. The working is carried out preferably with an excess in base, which amounts to about 2.5-3.5 mol.

The solvents which are to be taken into consideration for the conversion of the initial materials are for instance benzene, acetone, ethyl alcohol, propyl alcohol, butyl alcohol, toluene, xylene, dioxane and higher boiling ethers such as propyl ether and butyl ether. It is well to carry out the working at increased temperature, and preferably at such temperatures which correspond to the boiling temperatures of the organic solvents which are used.

Although β -bromide- α -tetralons are generally employed as initial materials, the corresponding chlorine and iodine compounds are also suitable, although these are less easily accessible.

The new compounds may be obtained also in such a manner, that not the hydrogenated heterocyclic nitrogen bases, but the unhydrogenated substances are brought to conversion. Instead of piperidine, for instance pyridine may be used. But in this instance it is necessary to hydrogenate the pyridine ring in the product obtained, which may be carried out for instance with employment of platinum as catalyst.

The amino ketone produced at the conversion is extracted with acids from the actually employed organic solvent. For the extraction diluted mineral acids such as hydrochloric acid, sulphuric acid or organic acids such as tartaric acid, citric acid and lactic acid may be used.

In the following the production of the new compounds will be explained on hand of some examples, without limitation of the invention to the materials, quantity proportions and temperatures employed in the examples being intended.

Example 1—1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphtalene

225 grs of β -bromine- α -tetralon (1.0 mol) are dissolved in 200 ccm benzene and this solution is added into a boiling solution of 260 grs piperidine in 300 ccm benzene. Strong reaction takes place immediately. 154 grs piperidine bromine hydrate=93% of the theory separate out at this occasion. From the benzolic solution the amino ketone is separated out by diluted acids, the acid extract is alkalisied and extracted out with benzol. The benzolic solution at the evaporation leaves behind 140 grs 1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphtalene=70% of the theory of the boiling point at 0.3 mm Hg 172°. The colourless chlorine hydrate, which is obtained according to usual methods by conversion with the stoichiometric quantity of hydrochloric acid, shows the melting point 220°.

Example 2—6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene

382 grs 6-methoxy-2-brom-1-oxo-1,2,3,4-tetrahydronaphthalene (1.5 mol) of the melting point 81° are dissolved in 600 ccm toluene, and this solution is poured into a boiling solution of 400 grs piperidine (4.7 mol) with 750 ccm toluene. After slight reaction piperidine bromine hydrate separates out soon. It is heated for some time on the water bath, then sucked off by the separated out piperidine bromine hydrate (240 grs=96.2% of the theory), and the amino ketone is extracted by diluted acids from the solution in toluene. From the acid solution the amino ketone is separated by diluted alkalis as thick oil taken up by an organic solvent such as benzol or ether, the residue remaining after the expelling of the solvent is distilled or directly worked to chlorine hydrate or to other salts. 325 grs 6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene (mol weight 259) of the boiling point 0.5 mm 195°=83.8% of the theory are obtained as thick oil, which solidifies to a crystalline mass. The colourless base can be re-crystallised from ether and then melts at 68°. The chlorine hydrate is produced therefrom according to usual methods and shows a melting and decomposition point of 202°.

Example 3—6-oxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene

85 grs 6-acetoxy-1-oxo-2-brom-1,2,3,4-tetrahydronaphthalene (=0.3 mol) are converted in benzol with 100 grs piperidine. After the usual treatment for the obtention of the amino ketone salt (compare example 1), 51 grs 6-oxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene are obtained. The chlorine hydrate has a melting point of 162°. The yield amounts to 60% of the theory.

A similar body is obtained by dealkylation of 6-methoxy- or 6-ethoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene, which can be obtained in a similar manner as the compound according to examples 1 and 2, by means of boiling 40-45% hydrobromic acid.

Example 4—6-methoxy-1-oxo-2-N-tetrahydroisoquinolyl-1,2,3,4-tetrahydronaphthalene

180 grs 6-methoxy-1-oxo-2-bromine-1,2,3,4-tetrahydronaphthalene (0.7 mol) are converted with 270 grs tetrahydroisoquinoline into 700 ccm xylene. 172 grs 6-methoxy-1-oxo-2-N-(tetrahydroisoquinolyl)-1,2,3,4-tetrahydronaphthalene are obtained in a yield of 80% of the theory of the melting point 130-132° (from acetone). The chlorine hydrate has a melting point of 215°.

Example 5—6-methoxy-1-oxo-2-N-(6-ethoxy-1-methyl-1,2,3,4-tetrahydroisoquinolyl)-1,2,3,4-tetrahydronaphthalene

77 grs 6-methoxy-1-oxo-2-bromine-1,2,3,4-tetrahydronaphthalene (0.3 mol) are converted boiling with 160 grs 6-ethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline in 400-500 ccm propyl alcohol. 58 grs 6-methoxy-1-oxo-2-N-(6-ethoxy-1-methyl-1,2,3,4-tetrahydroisoquinolyl)-1,2,3,4-tetrahydronaphthalene are obtained in a yield of 55% of the theory of the melting point 130°. The chlorine hydrate has a melting point of 192°.

Example 6—6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene

38 grs 6-methoxy-2-bromine-1-oxo-1,2,3,4-tetrahydronaphthalene (0.15 mol) are dissolved cold with 40 grs piperidine (0.47 mol) in 150 ccm ace-

tone and the temperature of the solution is maintained at 20° by cooling. After some time 23 grs piperidine bromine hydrate=93% of the theory separate out. The acetone solution is worked up to amino ketone according to example 1. 23 grs 6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene of the boiling point 172° at 0.2 mm Hg are obtained. The melting point of the substance re-crystallised from ether amounts to 68°. The chlorine hydrate has a melting point of 202°. The yield amounts to 59% of the theory.

Example 7—6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene

38 grs 6-methoxy-2-bromine-1-oxo-1,2,3,4-tetrahydronaphthalene (0.15 mol) are dissolved warm in 150 ccm alcohol and poured into a boiling solution of 40 grs piperidine (0.47 mol) and 150 ccm alcohol. After boiling for one hour the working is carried out as in example 1. 27 grs 6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene of the boiling point 172° at 0.2 mm Hg are obtained. The melting point amounts to 68°. The chlorine hydrate has a melting point of 202°. The yield amounts to 70% of the theory.

Example 8—6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene

20 grs 6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-pyridinium bromide (0.06 mol) of the melting point of 250°, produced from molecular quantity 6-methoxy-1-oxo-2-bromine-1,2,3,4-tetrahydronaphthalene and pyridine in xylene, are catalytically hydrogenated in methylalcoholic solution with platinum as catalyst. After a rapid absorption of 0.18 mol hydrogen, the hydrogen absorption comes to standstill. When working up the reaction solution to amino ketone according to example 1, 14.5 grs 6-methoxy-1-oxo-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene of the boiling point 172° at 0.2 mm Hg are obtained. The melting point amounts to 68°. The chlorine hydrate has a melting point of 202°. The yield amounts to 93% of the theory.

Example 9—6-methoxy-1-oxo-2-N-α-pipecolyl-1,2,3,4-tetrahydronaphthalene

51 grs 6-methoxy-1-oxo-2-bromine-1,2,3,4-tetrahydronaphthalene (0.2 mol) are converted in a boiling dioxane with 60 grs α-pipecoline (0.6 mol). 35 grs α-pipecoline bromine hydrate (98% of the theory) separate out. When completing the working up of the reaction solution to amino ketone, 33 grs 6-methoxy-1-oxo-2-N-α-pipecolyl-1,2,3,4-tetrahydronaphthalene of the boiling point 192° at 1.6 mm Hg are obtained. The chlorine hydrate has a melting point of 192°. The yield amounts to 60% of the theory.

Example 10—7-methyl-1-oxo-2-N-(2'4'-dimethyl)piperidyl-1,2,3,4-tetrahydronaphthalene

141 grs 7-methyl-1-oxo-2-bromine-1,2,3,4-tetrahydronaphthalene (0.59 mol) are converted with 200 grs 2,4-dimethyl-piperidine (1.77 mol) in 450 ccm n-propyl ether (or n-butyl ether). 168 grs bromine hydrate of the 2,4 dimethylpiperidine (93.5% of the theory) are obtained. Of amino ketone are obtained 80 grs 7-methyl-1-oxo-2-N-(2'4'-dimethylpiperidyl)-1,2,3,4-tetrahydronaphthalene of the boiling point 165° at 0.25 Hg. The yield amounts to 50% of the theory. The chlorine hydrate has a melting point of 220° under decomposition.

Example 11.—7-methoxy - 1 - oxo - 2- N(2'4'-dimethyl) piperidyl-1,2,3,4-tetrahydronaphtalene

128 grs 7-methoxy -1- oxo -2- bromine-1,2,3,4-tetrahydronaphtalene (0.5 mol) of the melting point of 84° are converted boiling with 170 grs 2,4-dimethylpiperidine (1.5 mol) in 370 ccm benzol. 93 grs bromine hydrate of the 2,4 dimethyl-piperidine (96% of the theory) are obtained. Of amino ketone are obtained 80 grs 7-methoxy -1- oxo-2-N(2'4'-dimethyl)piperidyl-1,2,3,4-tetrahydronaphtalene of the boiling point 163° at 0.3 mm Hg. The yield amounts to 56% of the theory. The chlorine hydrate has a melting point from 198 to 200° under decomposition.

Example 12.—6-methoxy - 1 - oxo - 2 - N(2'4'-dimethyl) piperidyl-1,2,3,4-tetrahydronaphtalene

255 grs 6-methoxy -1- oxo -2- bromine-1,2,3,4-tetrahydronaphtalene (1.0 mol) are converted boiling with 270 grs 2,4-dimethylpiperidine (2.4 mol) in 800 ccm toluene. 97% of the theory are obtained in amino bromine hydrate. By means

of tartaric acid solution of amino ketone are isolated 287 grs 6-methoxy -1- oxo -2- N(2'4'-dimethyl)piperidyl - 1,2,3,4 - tetrahydronaphtalene (75% of the theory) of the boiling point 180° at 0.36 mm Hg. The chlorine hydrate has a melting point of 203° under decomposition.

Example 13.—1-oxo-2-N(2'4'-dimethyl) piperidyl - 1,2,3,4-tetrahydronaphtalene

225 grs β -bromine- α -tetralon (1 mol) are converted with 300 grs 2,4-dimethylpiperidine (2.65 mol) in 1000 ccm xylene at 120°. 186 grs bromine hydrate (96% of the theory) are isolated. The amino ketone is extracted by means of citric acid solution. 103 grs 1-oxo-2-N-(2'4'-dimethyl)piperidyl-1,2,3,4-tetrahydronaphtalene (40% of the theory) of the boiling point 158° at 0.2 mm Hg are obtained. The chlorine hydrate has a melting point of 232° under decomposition.

GEORG SCHEUING.
BRUNO WALACH.

ALIEN PROPERTY CUSTODIAN

RESINOUS CONDENSATION PRODUCTS

Werner Zerweck and Max Schubert, Frankfurt
am Main-Fechenheim, Germany; vested in the
Alien Property Custodian

Application filed January 18, 1940

Our present invention relates to resinous condensation products more particularly to those obtained by condensing with aldehydes, such as aliphatic aldehydes of a low molecular weight, particularly with formaldehyde, or with agents setting free such aldehydes, compounds containing a five-membered heterocyclic ring having two double bonds and, attached to the ring members at least one hydrogen atom and a member of the group consisting of a hydrogen atom and a group which can be condensed with aldehydes, but at the most two methine groups (CH) and one amino group.

The reaction may be carried out with or without the addition of a diluent. Generally the addition of an acid agent accelerates, that of an alkaline acting agent retards the condensation reaction. According to the reactivity of the component to be condensed one may regulate the course of reaction to the desired degree by means of the addition either of acid or alkaline acting agents.

The condensation may be carried out in several steps and the soluble alkylol compound may be isolated.

Moreover, other compounds which can be condensed with aldehydes such as urea and its derivatives, such as thiourea, N-substituted ureas, guanidine, dicyandiamide, amines of six- and five-membered heterocyclic ring systems, such as melamine, diaminopyrimidine, phenyl-guanazole or the corresponding hydrazine compounds, sulphonamides, mono- and polycarboxylic acid amides, anilines, phenols and the like may be added to the reaction components so that it is possible to vary the properties of the reaction products in different directions. The present condensation products are resinous products mostly like the phenol-formaldehyde condensation products and are hard in the heat, infusible and insoluble in all the usual solvents, and exhibit considerable mechanical strength and chemical resistance.

Compared with the phenol-formaldehyde condensation products they are distinguished by a particular resistance to boiling water and acids and alkalis, a fact which is perhaps due to the absence of free hydroxyl groups, which are present in the molecule of the phenol-formaldehyde condensation products.

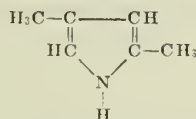
The new products of the present invention may be applied for the manufacture of plastic masses, moulding masses, adhesive and glueing agents, lacquers, films and other artificial products.

Moreover, it is possible to mix the present resinous condensation products with other natural and artificial resins such as phenol, urea, aminotriazine, aniline, alkyl or ketone resins.

The following examples illustrate the invention, the parts being by weight.

Example 1

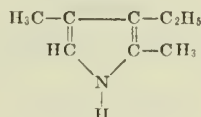
A mixture of 10 parts of 2,4-dimethylpyrrole of the formula:



50 parts of a formaldehyde solution of 30% strength and 50 parts of alcohol is heated under reflux for a short time and the clear solution is evaporated to dryness. The reaction product is a dark and opaque resin which is insoluble in water and organic solvents.

Example 2

To a solution of 5 parts of 2,4-dimethyl-3-ethylpyrrole of the formula:



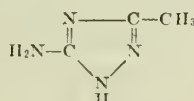
(cf. H. Fischer, Ber. vol. 56, page 612), in about 25 parts of alcohol, 25 parts of a formaldehyde solution of 30% strength and 1 part of concentrated hydrochloric acid are added and the mixture is evaporated on the water-bath to dryness. In this manner a dark and opaque resin is obtained which is hardened by long heating at 90 to 100°C or a shorter heating at 120 to 130°C.

Example 3

10 parts of a trimethylpyrrole mixture, obtained by acting with methyl iodide on potassium 2,4-dimethylpyrrole, are dissolved in about 50 parts of alcohol, 50 parts of a formaldehyde solution of 30% strength are added and the mixture is heated for a short time on the water-bath under reflux. The dark red solution is evaporated at 90 to 100°C and then heated for some hours at 120 to 130°C. The reaction product is a hard and dark resin.

Example 4

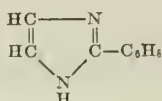
10 parts of 3-methyl-5-amino-1,2,4-triazole of the formula:



are dissolved in 30 parts of a slightly warmed formaldehyde solution of 30% strength. After evaporation on the water-bath a clear soft resin remains, which can be hardened by heating at 110 to 130°C.

Example 5

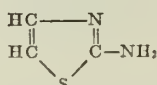
A mixture of 7.2 parts of phenylimidazole(2-phenylglyoxaline) of the formula:



3 parts of urea, 3.5 parts of hexamethylenetetramine and 20 parts of an aqueous formaldehyde solution of 30% strength is warmed for some hours at 90 to 100°C under reflux and then evaporated to dryness. The reaction product is converted into the final state by heating for some hours at 130–140°C. It is then a water insoluble resin.

Example 6

10 parts of 2-aminothiazole of the formula:

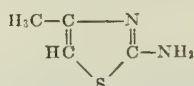


(cf. Traumann, Liebig's Annalen, vol. 249, page 36) are dissolved in about 50 parts of alcohol; 20 parts of benzaldehyde and 1.5 parts of concentrated hydrochloric acid are added and the mixture is heated for a short time on the water-bath under reflux. After evaporation to dryness the resin formed is heated at 120 to 130°C until it becomes hard.

When replacing benzaldehyde by 50 parts of a formaldehyde solution of 30% strength a resin of similar properties is obtained.

Example 7

10 parts of 4-methyl-2-aminothiazole of the formula:



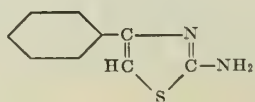
are dissolved in 50 parts of a slightly warmed formaldehyde solution of 30% strength. After addition of 4 parts of concentrated hydrochloric acid the clear reddish solution is evaporated to dryness and the dark residue is heated to 120 to 130°C for hardening. In this manner a dark and hard resin is obtained which is resistant to water and benzene and particularly suitable for the manufacture of adhesive and glueing agents.

Example 8

10 parts of 4-methyl-2-aminothiazole are dissolved in 50 parts of a warmed formaldehyde solution of 30% strength. To this solution while stirring slowly at 90 to 100°C a mixture of 40 parts of butanol and 20 parts of toluene is added. When the water has been removed by an azeotropic distillation, a clear viscous solution of the reaction product in butanol is obtained. On pouring such a resin solution on a glass or metallic support, after drying a transparent water-repellent coating is obtained, which by standing for a long time or by warming at elevated temperatures can be hardened and is in this state resistant to water, benzene and alcohol.

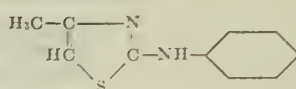
Example 9

To a hot solution of 10 parts of 4-phenyl-2-aminothiazole of the formula:



50 parts of a formaldehyde solution of 30% strength and 2 parts of formic acid are added and the mixture is evaporated to dryness. The residue is heated for a short time at 130 to 140°C for hardening. A yellowish resin is obtained, which is insoluble in water and organic solvents.

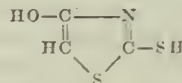
By replacing the 4-phenyl-2-aminothiazole by the same amount of 4-methyl-2-phenylaminothiazole of the formula:



a similar resin likewise of good properties is obtained.

Example 10

10 parts of 2-mercapto-4-hydroxythiazole of the formula:



(cf. Journ. f. prakt. Chem., vol. 16, page 1) are dissolved in about 50 parts of a formaldehyde solution of 30% strength while warming on the water-bath. After the addition of 2 parts of formic acid the clear orange solution is evaporated to dryness. The residue is shortly heated at 120 to 130°C. In this manner a clear orange resin, which is insoluble in water, benzene and alcohol, is obtained.

Example 11

The solution of 30 parts of 2-amino-4-methylthiazole (cf. examples 7 and 8) in about 20 parts of a formaldehyde solution of 40% strength is evaporated to dryness at 90 to 100°C. The residue is heated for some hours at 120 to 130°C. In this manner there is obtained a slightly colored resin which is very resistant to water and insoluble in benzene and alcohol.

Example 12

The solution of 2-amino-4-methylthiazole in a formaldehyde solution as obtained according to the foregoing example is shortly warmed until after cooling to room temperature a viscous solution is formed to which 5 parts of a hydrochloric acid of about 20% strength are added.

By coating, for instance, a beech veneer sheet of 2 mms strength on both sides with the aforesaid solution, covering each side with a further beech veneer sheet of the same strength but not coated with solution, in such a way that the woody fibers of the exterior sheets are running in a direction which is rightangled to that of the fibers of the interior sheet, and by bringing this layer of sheets into a veneering press which has been heated previously to about 100°C and pressing the sheets for about 10 minutes under a pressure of 10 to 20 atmospheres, a ply-wood sheet is obtained which is resistant to water even when boiled therein for some hours.

Example 13

100 parts of an alkyd resin obtained by heating at 240° C for about 6 hours a mixture of 280 parts of 9.11-oktadiene acid, 125 parts of glycerine and 225 parts of phthalic acid anhydride are dissolved in about 60 parts of toluene. To this solution there are added 160 parts of a solution of 50% strength in butanol or isobutanol of a condensation product obtained by condensing, according to example 8, 2-amino-4-methylthiazole and butanol or isobutanol with formaldehyde

The lacquer thus formed may be dried during about 1 hour at 175–180° C and yields coat-layers, which are very resistant to motor oils and boiling water.

Example 14

100 parts of an alkyd resin, obtained according to the process as described in British specification No. 316.914 by acting with phthalic acid anhydride on a mixture of linseed oil fatty acid mono-glyceride and glycerole, are dissolved in about 100 parts of toluene and 140 parts of a solution of 50% strength of a 2-amino-4-methyl thiazole butanole-(isobutanole)-formaldehyde condensation product are added. After having been dried at 180° C the mixture is a coat-layer resistant to motor oils.

Example 15

100 parts of an alkyd resin, obtained by heating a mixture of aliphatic carboxylic acids obtained by saponifying palm oil with glycerine and phthalic acid anhydride, are dissolved in about 100 parts of toluene and 200 parts of the thiazole formaldehyde resin solution as used in examples 13 and 14 are added. The lacquer may be dried by heating at 200° C for half an hour and is then

particularly elastic and resistant to motor oils, boiling water and dilute alkalies.

Example 16

5 10 parts of 2-amino-4-methylthiazole are dissolved in 27 parts of a formaldehyde solution of 30% strength, then 40 parts of n-butanole are added and the solution is heated until distillation begins. Then 20 parts of toluene are added and by azeotropic distillation about 20 parts of water are removed, 1 part of phthalic acid anhydride is added and the distillation is continued until no more water passes over. A clear viscous butanolic solution of the reaction product is obtained. When pouring such a resin solution on a glass or metal surface after drying a transparent, water repelling coat is obtained which can be hardened by standing for a longer time or warming at higher temperatures. Then it is resistant to water, benzene and alcohol.

20 When replacing n-butanol by the same quantity of isobutanol a lacquer solution of similar properties is obtained.

WERNER ZERWECK.
MAX SCHUBERT.

ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCTS AND A PROCESS OF PRODUCING SAME

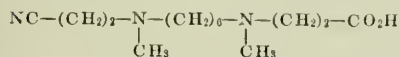
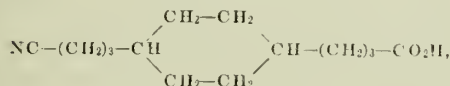
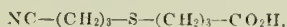
Hugo Kroeper, Heidelberg, and Hans Haussmann, Mannheim, Germany; vested in the Alien Property Custodian

No Drawing. Application filed January 22, 1940

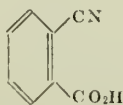
The present invention relates to a process for the production of condensation products.

We have found that condensation products suitable for a wide range of applications are obtained by causing mononitriles which besides the nitrile group contain a carboxylic group in the molecule, to react at elevated temperature with amines containing in the molecule at least two amino groups bearing at least one hydrogen atom directly attached to the amino nitrogen, i. e., primary or secondary amino groups. A treatment with hydrating agents may be carried out during or after the reaction. The carboxylic group may be present in the free or in a modified state, i. e. there may be employed the free nitrile carboxylic acids, themselves as well as for example their esters, anhydrides, halides, amides or thioamides. When a simultaneous or subsequent treatment with hydrating agents is desired it is advantageous to start from the nitrile carboxylic acids themselves. When the products are to contain the nitrogen of the nitrile group wholly or partially combined, it is advantageous to employ such derivatives of the nitrile carboxylic acids as neither split off water nor alcohols during the reaction.

Suitable nitrile-carboxylic acids are, for example, those which have the nitrile group and the carboxyl group linked to one another by one or more carbon atoms. The carbon skeleton of the nitrile carboxylic acids may be of aliphatic, cycloaliphatic, mixed aliphatic-aromatic or aromatic character; if desired, it may be interrupted by hetero atoms or groupings comprising hetero atoms. Compounds of the following formulae are given as examples of suitable nitrile carboxylic acids:

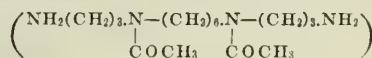


and

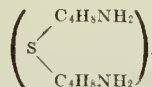


Among suitable amines we may mention for example pentamethylenediamine, hexamethylenediamine, 1,4-cyclohexyldiethylamine, p-phenylene-bis-ethylamine, triethylenetetramine, ben-

zidine, aminoethylpiperazine, N,N'-di-(acetylpropylamino)-hexamethylenediamine



and thiodibutylamine



The reaction is carried out at elevated temperatures, which may range for example up to about 300°C, advantageously at temperatures of between 150° and 300° C, varying according to the type of the initial materials used and the nature of the products desired. By prolonged heating and employment of high temperatures high-molecular products are obtained. In many cases it is preferable to conduct the reaction in closed vessels, especially in case the condensation is carried out at temperatures above the boiling point of one or both of the initial substances.

The quantities in which the initial substances are used may be varied within wide limits. Usually 1 molecular proportion of diamine is used to about 1 molecular proportion of nitrile carboxylic acid or 2 molecular proportions of an amine having 3 primary or secondary amino groups are used to about 3 molecular proportions of nitrile carboxylic acids etc. By using one of the initial substance in excess, the length of the chain of the condensation products may be varied and more or less highly polymerized products obtained. In many cases it is useful to subject the polymerized products to heat treatment in vacuo.

If a treatment with hydrating agents be carried out during or after the condensation, polyamides are formed, ammonia or ammonium salts being split off.

Among hydrating agents we may mention, for example, water which may be added as such or generated by a simultaneous reaction attended with the formation of water; thus carboxylic acids or alcohols may be heated together with the initial substances from which water is split off upon reaction with the amine used.

The following example serves to illustrate how the present invention may be carried out in practice, but the invention is not restricted to this example; the parts are by weight.

Example

113 parts of gamma-cyanobutyric acid and 116 parts of hexamethylenediamine are slowly heated to 160° C with reflux cooling; a vigorous evolution of ammonia takes place. The temperature is then slowly raised to 290°C and heating continued at this temperature for another 12 hours until the evolution of ammonia is completed. The product obtained shows properties similar to those of polyamides.

HUGO KROEPER,
HANS HAUSSMANN.

ALIEN PROPERTY CUSTODIAN

EXTRACTION OF GELATINE FROM OSSEIN

Holger Jørgensen, Copenhagen, Denmark; vested
in the Alien Property Custodian

Application filed January 25, 1940

This invention relates to a method of producing gelatine from ossein, i.e. the substance of bones deprived fully or substantially from mineral constituents and, if so desired, from fats. The method by which gelatine has hitherto normally been produced from ossein is as follows:

The ossein is soaked or washed with water at normal temperatures in order to remove the residue of acid which may be present therein and after this the ossein is immersed in milk of lime changed at suitable intervals. After having been lime treated for 1 to 2 months or more the lime treated mass is thoroughly washed with water. The last residues of the lime contained therein are removed by washing with acid and the acid is again removed by washing with water in order to produce a neutral product which by extraction with hot water in, say, 3 or 4 subsequent treatments, can be converted into gelatine.

The prolonged lime treatment constitutes a substantial drawback in the utilisation of ossein as a raw material for gelatine in view of the long duration of the process as well as because part of the gelatine forming proteins of the ossein will dissolve in the milk of lime and consequently be lost. The lime treatment has, however, been necessary because ossein that has not been treated by lime can be extracted only very slowly by water and because in this case there will not be produced gelatine but glue having a very bad gelatinating power.

I have found, however, that the lime treatment and the drawbacks resulting from this treatment can be wholly or substantially omitted by suitably controlling the pH during the extraction. Extensive investigations have revealed the fact that within a certain field of pH in the extraction fluid the conversion of the ossein into gelatine is produced with extreme slowness if the ossein has not been subjected to the lime treatment mentioned above. On the other hand the velocity with which the extraction can be carried out increases very rapidly when extraction fluid is used, the pH of which is outside the said field of pH. The said field of pH in which the extraction proceeds very slowly is within the pH range of abt. pH 5 to pH 8 and thus this field comprises the neutral reaction used in the extraction as employed hitherto which explains the old experience that the extraction of gelatine from ossein is generally impossible unless the ossein has been previously treated by lime.

With this general statement of the object of my invention I will now proceed to describe the embodiment thereof and the manner in which

my invention is carried out, and it will be understood that while I have described what may be considered as a preferable embodiment of my invention, I do not limit myself to the precise conditions or proportions herein set forth as they may be varied by those skilled in the art in accordance with the particular purposes for which they are intended and the conditions under which they are to be utilised.

In the preferred embodiment of my invention the ossein is subjected to extraction at temperatures exceeding 50°C. by means of an aqueous extraction fluid, the pH of which is outside the field of pH within which the extraction of gelatine from ossein that has not been lime treated is extremely slow. The extraction may be repeated several times. The extract which may be concentrated by evaporation during or after the extraction process is then caused to gelatinate in the usual manner and the gelatinated product is dried. The ossein is preferably soaked before the extraction.

The position of the field of pH within which the extraction of ossein that has not been lime treated is extremely slow and the importance of taking it into consideration will appear from the drawing showing an example of the relation between the pH value of the extraction fluid and the proportion of gelatine resulting from the extraction, the ordinate representing the yield obtained in the extraction of a certain not lime treated ossein under defined conditions at the pH given by the abscissa. From the curve it appears clearly that relatively very small proportions of ossein only are dissolved during the pre-determined period of treatment at pH values between 5 and 8. At pH values below 5 or above 8, on the contrary, it is possible to dissolve a much greater part of the ossein under the given conditions. The curve represents the results of a particular experiment with a particular ossein product and may vary in its shape and position in the case of varying samples of ossein but the curve is typical in the respects mentioned above, i.e. as far as concerns the existence of the pH field in which the extraction is extremely slow and with respect to said field being positioned within the range of pH 5 to pH 8 as well as with respect to the marked rise of the curve outside said field.

It will be found that the unity in which the ordinate is to be measured is not given in order that the curve shall be a typical one, the extracted proportion represented by the ordinate depending of course upon the time of treatment,

the temperature and the apparatus used for the extraction. The influence of these circumstances is, however, well known. Thus it is generally known that only small yields can be obtained at temperatures below abt. 60°C. An extraction temperature of 50°C. may in fact be considered the lower limit at which the extraction can be practically carried out. Generally, extraction temperatures of abt. 70–80°C. are used. A number of examples of coordinating values of temperature, time and yield are given in the following to enable the position of the curve to be estimated. The exact position of the curve, as mentioned above, will also depend upon other circumstances but it is not necessary to know the position of the curve in order to be able to carry out the process in question as the only fact which it is necessary to know is the position on the pH axis of the field of pH within which the extraction of non-lime treated ossein is too slow to be practically utilised.

When extracting one part of ossein soaked two days in water at normal temperature with 3.5 parts of an extraction fluid consisting of water and the quantity of acid (HCl) or alkali (NaOH) necessary for obtaining and maintaining the pH given, the following yields calculated as per cent of the weight of ossein are obtained in 5 hours at 76°C.:

pH.....	3	3	4.4	4.6	4.9	6	7	9	11
Yield%.....	64.5	37.1	23.6	18.3	12.8	9.4	9.8	15.9	54.3

On extracting in 5 hours at 60° by various buffer solutions ossein pretreated in the same manner the following yields are obtained at the pH values stated.

pH.....	3.5	4.8	4.9	6.0	7.0	8.0
Yield.....	11.6	3.9	4.4	3.6	3.7	4.5

From ossein soaked one day at ordinary temperature, by extraction with water with addition of NaOH so as to maintain pH between 9.6 and 10 48% gelatine is obtained in 6 hours at 80°C. On extracting the residue of the ossein by another quantity of extraction fluid at the same pH and the same temperature for 6 hours, further 45% could be obtained. By treating 1 part of ossein by 3.5 parts of N/50 hydrochloric acid whereby pH will change during the extraction period from pH 3.5 to pH 4.5, 34.7% gelatine is obtained in 6 hours.

When carrying out the process any kind of ossein can be used; thus for instance the kind of ossein on sale produced from bones which have been deprived of fat by one or other method, for instance by an extraction with organic fat solvents, or the kind produced from bones treated by the sundrying method used in India, are both well suited. The bones may have been deprived completely or almost completely of their contents of calcium phosphate and calcium carbonate by maceration with hydrochloric acid or by the treatment with sulphurous acid or in other known manner. Even the kinds of ossein which have been subjected to known pretreatments in order to increase the solubility thereof are employable for the purpose of my present invention, for instance the ossein which has been subjected to a treatment by peroxides.

If the ossein is not subjected to extraction in accordance with the present invention immediately when it has been produced, I prefer to subject it to a pre-treatment to make it more accessible to the influence of the extraction fluid.

Thus, in case of the ossein of commerce, I prefer to wash or soak it by water. There would be no objection to subjecting the ossein to a more or less extensive treatment by lime. The particular advantage of my present method, however, consists in that such treatment with lime need not be of so long a duration as in the known processes or can be completely omitted, which I prefer.

After this the ossein is subjected to an extraction process which is carried out in the wellknown manner with the exception of the pH prevailing during the same. The pH to be considered is the one prevailing in the liquid in contact with the ossein or the part thereof which has not yet been dissolved. Consequently it is not sufficient in all cases to control pH of the liquid poured over the ossein or in which the ossein is immersed because the pH may change considerably under the influence of the ossein, for instance when the same is not quite neutral. Consequently a control of pH is in some cases carried out to advantage during the extraction process itself by adding an acid or a base, for instance in such a manner that the pH value is maintained constant during the whole extraction process or during a substantial part thereof. Alternately I add a suitable buffering substance to the extraction fluid. I prefer to carry out the extraction in two or more stages using for one or more of the extraction operations or for all of them an extraction fluid, the pH of which is outside the field of pH 5 to pH 8 within which the extraction proceeds with extreme slowness.

Although, as it is well known, the gelatinating power of the gelatine is destroyed under the influence of particularly high or low hydrogen ion concentrations, I have found that there are intervals of pH within which the extraction can be safely carried out in order to obtain a good gelatinating power simultaneously with a great velocity of the conversion of the ossein to gelatine and a great yield of gelatine. These intervals are defined by pH being not less than abt. 2 and not greater than abt. 12, at the same time avoiding the field of pH from pH 5 to pH 8 in which the extraction is slow. Within the intervals of pH from pH 2 to pH 5 and from pH 8 to pH 12 a satisfactory extraction of gelatine can, however, be obtained in accordance with the present invention.

The extract or extracts obtained are treated in the normal manner, i. e. after concentration, if necessary, and purification in the wellknown manner, if so desired, they are caused to gelatinate by cooling and then dried.

In one particular case I have soaked dry ossein of the commerce with water for one day at ordinary temperature and after removing the water, that has not been taken up by the ossein, I have placed 150 kgs thereof in an extraction vat of the kind normally used for extracting gelatine-producing raw materials. 500 litres of water at 75° C. were then poured over the ossein. After this, hydrochloric acid was added until pH in a sample of the liquid was found to be abt. 3.5. After treatment for 4 hours at the said temperature the extract was removed and another 500 litres of water were poured upon the undissolved residue of the ossein. The liquid was adjusted to pH=abt. 3 and after treatment for 4 hours the extract was removed. The procedure was repeated until 4 or 5 extractions had been made, pH being between 3 and 3.5 during each extraction. In 4 or 5 extracting operations in this

manner 85% of the ossein was obtained in the extracts in the form of gelatine.

In another particular case I have carried out the extraction in the same manner with the only exception that pH during all the extraction operations was adjusted to a value between pH 9.5 and pH 10. In 4 or 5 extraction operations each of which was of a duration of about 5 hours, the proportion of gelatine corresponding to about 90% of the weight of the ossein was obtained in solution.

In the preceding descriptive part of the specification and in the claims, when the pH value is mentioned, the same is supposed to be determined in the liquid after the same has been cooled to about 15-30° C. Thus pH does not mean the values thereof, that could be determined if the hot extraction fluid was subjected to a pH determination without being previously cooled.

HOLGER JORGENSEN.

PUBLISHED

APRIL 20, 1943.

BY A. P. C.

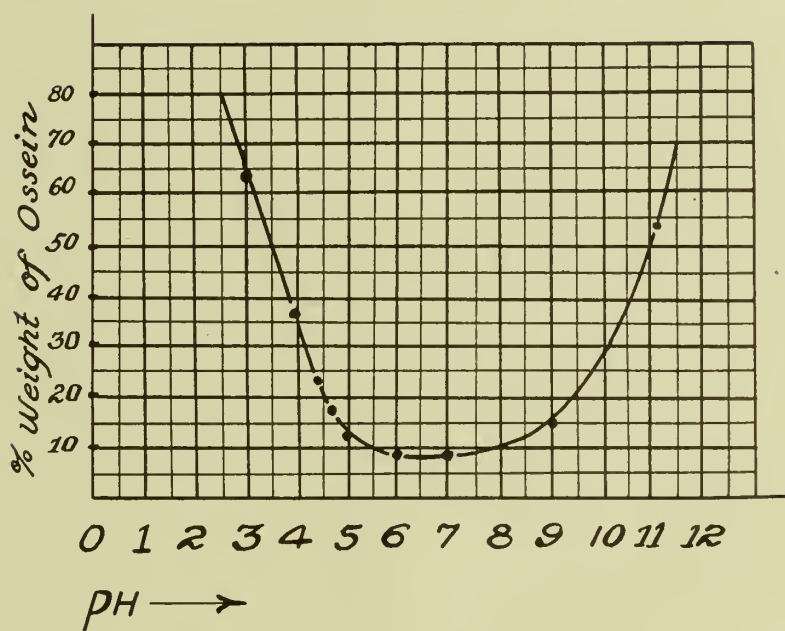
H. JØRGENSEN

EXTRACTION OF GELATINE FROM OSSEIN

Filed Jan. 25, 1940

Serial No.

315,627



Inventor,
H. Jørgensen

By: Glascock Downing & Seibold
Attys.

ALIEN PROPERTY CUSTODIAN

PROCESS OF MAKING VANILLIN FROM LIGNIN, LIGNIN DERIVATIVES OR OTHER MATERIALS CONTAINING LIGNIN

Karl Freudenberg and Willy Lautsch, Heidelberg,
and Hans Brenek, Mannheim, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed February 10, 1940

This invention relates to a process of making vanillin from lignin, derivatives of lignin or other materials containing lignin.

The production of vanillin from materials containing lignin as used in practice can theoretically be explained from the formula for the constitution of lignin, as far as such formula is known. The commercial production of vanillin from lignin raw materials, however, had to be kept within narrow limits which in the first place is probably due to the fact that with all methods so far known for carrying out this process the attainable yields are relatively small and amount to only a very small fraction of the theoretical yield.

It is further known that vanillin may be produced from lignin sulpho-acids, the main constituents of sulphate cellulose waste-lye. In this case the process may for instance, be carried out in such a way that the sulphite waste lye which had been made strongly alkaline by ample addition of lime or caustic alkali is heated for some longer time to a temperature from 160 to 180° and that the vanillin formed is isolated by extraction with a suitable organic solvent (for instance benzol). However, the yield attained by means of this process is relatively very small and as a rule will only be 2 to 3 percent and in most favorable cases about 6 percent of the lignin used. (In accordance with this is also the statement "between 1 and 2.4 g per liter" which is found in Hägglund's book "Holzchemie", second edition, 1939, page 165, last line, the sulphite waste lye containing approximately 40 g of lignin per liter. See also the periodical "Holz als Roh- und Werkstoff" 1931, No. 1, page 20, right-hand column, stating that "there may be figured with a vanillin yield of about 5 to 6 percent of the weight of the lignin".) Other allegedly much higher yields occasionally given in the older literature were later found to be based on grave errors mainly due to improper methods of determining the vanillin.

It is further remarkable that as lignin raw material for the production of vanillin hitherto solely sulphite cellulose waste-lye, that is lignin sulpho-acids, had been used and that it has not been possible to produce yields of vanillin or of vanillin derivatives sufficient for commercial purposes from other lignin substances (for instance from wood saccharification residues or from lignin isolated from wood by means of copper oxide ammonia or directly from wood or lignified vegetable matter or finally from derivatives of lignin.)

There has been no doubt that the process leading from lignin to vanillin is a process of oxidation. Accordingly it had been tried to expedite the process by introducing air or oxygen or by applying oxygen discharging or oxygen transmitting substances. However, no better yields could be obtained when carrying out the process in such a way. In the contrary, the cited book of Hägglund at the above cited place, for instance, states that "introduction of air had an unfavorable effect on the yield of vanillin."

The reason for these unsuccessful attempts, as careful tests have proven, was found to reside in the fact that the hitherto used processes of oxidation with the selected oxidizing agent or improper working conditions (temperature, and time of reaction) are either insufficient to attack the structure of the lignin or that too strong an action is exerted, with the result that the waste products first formed (phenols, oxy-acids, oxy-aldehydes etc.) are subject to further destruction. It has also been found that by carrying on the process under proper working conditions there may be attained considerably higher yields, eventually even a yield twice as large as hitherto obtainable, or also the same yields in a more convenient way and at smaller costs; furthermore, it has been found that like yields of vanillin may be produced, besides from cellulose waste lye, from the other above mentioned lignin raw materials.

The working conditions which are suitable for the present purpose from the basis of our new process. This process consists therein that the lignin raw material is heated in the presence of alkali (lime, caustic alkali) to a moderate temperature of 100 to 110°, in no case more than about 140°, under simultaneous action of finely distributed oxygen and/or oxygen discharging or oxygen transmitting compounds. Accordingly, air or a current of oxygen gas in fine distribution may be used at the stated temperatures either alone or in the presence of oxygen discharging or oxygen transmitting compounds. Such compounds may also be used alone (that is without introduction of air) in order to react onto the lignin raw material. In many cases the favorable action of the metal oxides may depend upon the surprising and hitherto unknown fact that several insoluble lignin raw materials readily enter into solution under the action of the metal oxides in the presence of alkali and thus are subject to a very uniform action of oxygen.

Heating of the reaction mass may be effected in accordance with prevailing conditions in an

open container or under reflux or also in a closed container under pressure. Especially good results have been attained by addition of salts raising the boiling temperature. As may be seen from Example 7 and the subsequent Table, the yield will increase with increasing temperature. As oxygen discharging or oxygen transmitting substances, above all the several inorganic oxygen compounds or salts that are more or less known for such reactions have been found to be suitable for the present purpose, especially the compounds that may relatively easily be reduced in alkaline agents (for instance nickel oxide, cobalt oxide, cerium oxide, lead oxide, MnO_2 , mangano-manganite, potassium ferri-cyanide etc.) Also gas-condensing adsorption substances, such as for instance active carbon, may well be used as oxygen transmitting substances (see Example 10).

The selection of the working conditions to be used in individual cases as well as of the oxygen transmitting substance etc. depend in the first place upon the kind and exterior condition of the raw material. Accordingly, the proper working conditions and oxygen transmitting substances may easily be ascertained in every case by a few trials. Thus, for instance, it has been found as being of advantage in certain cases to subject the lignin raw material first to a preliminary boiling with alkali (lime, caustic potash or caustic soda) and thereupon to heating with oxygen metal oxides or the like in the presence of alkali (see Examples 8 and 9).

The working-up of the reaction mixture and the isolation of the vanillin is carried out in known manner, particularly as indicated in the examples given hereinafter.

A great advantage of our new process consists therein that the oxygen discharging or oxygen transmitting substances may easily be recovered and again be used with the materials to be subsequently treated.

As above stated, as oxygen transmitting substances there may also be used adsorption substances which owing to their large surfaces act condensing upon gases. As such "activators" there may be used, for instance, active carbon, platinum-sponge, finely distributed palladium and the like.

It has surprisingly been found that with a sufficiently fine distribution of the lignin material offering a greater surface of action to the oxygen high yields of vanillin may be attained under definite conditions also without addition of a special activator. For this purpose the lignin raw material is heated in a distribution as fine as possible, for instance in the form of finely powdered lignin or finely ground wood-flour in the presence of alkali under simultaneous action of oxygen (oxygen of the air) and under pressure to a moderately high temperature (not over 140°), while the isolation of the formed vanillin is preferably carried out in the above described manner.

It has furthermore been found that the yields may be essentially increased (for instance as far as to a double or quintuple value or more of the hitherto attainable yields), if the lignin raw material is heated under proper conditions in the presence of free alkali with aromatic nitro-compounds. The most suitable conditions (alkali concentration, temperature and time of heating, as well as the used quantity of the nitro-compound) depend mainly upon the kind of the lignin raw material and may easily be ascertained

in every case by means of a few trials with the respective raw material.

Thus, for instance, for a definite raw material (cuproxamlignin) it has been found that the yield increases with the applied temperature and that upon surpassing a definite temperature (160°) the yield does not further increase or finally again decreases. A further comparative test has shown that with a boiling time of 72 hours (at 103°) more than the double yield was obtained, as compared with the yield obtained under otherwise like conditions with a boiling time of only 24 hours. Further information may be found in the examples given hereinafter.

Example 1

5 kg of lignin (consisting of finely comminuted pine-wood, isolated in known manner by means of highly concentrated muriatic acid or by treatment with copper oxide ammonia) were mixed with 50 liters of a 10% potash lye and cobalt hydroxide precipitated from 5 kg of cobalt sulphate in the presence of hydrogen peroxide with hot soda lye, heated under reflux and intensive agitation for 24 hours, and finely distributed oxygen passed through the mixture. Upon completion of the boiling the cobalt hydroxide is separated by a centrifuge, the substance still absorbed by the hydroxide removed by stirring several times with dilute lye, and carbonic acid introduced into the united liquids, until the caustic potash is converted into bicarbonate. The vanillin is thereupon withdrawn by extraction with ether, methylene chloride, benzol or the like and purified upon volatilization of the solvent, eventually by re-crystallisation. There are obtained 400 g of pure vanillin, that is 8 percent of the used lignin. From the bicarbonate-alkaline solution 100 g of vanillin acid, that is a yield of 2 percent may be obtained after acidulation and renewed extraction.

Example 2

5 kg of lignin (the same as in Example 1) are boiled with 50 liters of a 10% potash lye with addition of 10 kg of lead dioxide. The working-up is the same as stated in Example 1; the yield is likewise about the same as stated in this example.

Example 3

2 kg of de-resinized pine-wood flour (corresponding to about 500 g of lignin) are mixed with 20 liters of a 10% potash lye and cobalt hydroxide precipitated from 2 kg cobalt sulphate in the presence of hydrogen peroxide with hot soda lye and heated under reflux for 24 hours and agitation, at the same time passing oxygen there-through. The reaction mixture is further treated the same as in Examples 1 and 2. This will furnish 45 g of vanillin, that is 9 percent with relation to the quantity of lignin contained in the used pine-wood. Besides, there may be obtained 10 g, that is 2 percent, of vanillin acid.

Example 4

2 kg of wood-flour are stirred-up in 20 liters of a 10% potash lye and mixed with freshly precipitated mangano-manganite obtained from the solution of 3 kg of $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ by precipitation with soda lye and subsequent oxidation with hydrogen peroxide or air or oxygen. The mixture is boiled for about 15 hours under reflux and agitation and at the same time air or oxygen is introduced in fine distribution. Thereupon separation from undissolved cellulose and the man-

gano-manganite is effected and the treatment continued with carbonic acid, until the caustic alkali is converted into bicarbonate, whereupon vanillin is withdrawn from the reaction mixture by extraction (with benzol or ether). This vanillin upon volatilization of the solvent will be obtained in beautiful crystalline form. The yield amounts to 40 g, that is 8 percent of the lignin contained in the wood material.

Example 5

1 kg of lignin bromide (obtained for instance in accordance with Ber. 1929, 62, page 1554) is stirred-up in 10 liters of a 10% potash lye and mixed with cobalt hydroxide obtained from 1 kg of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in the presence of hydrogen peroxide by precipitation with hot soda lye. The mixture is heated under reflux to boiling temperature for about 24 hours and oxygen simultaneously passed therethrough. The lignin bromide will be fully dissolved and converted into vanillin 6-bromide.

The reaction mixture is thereupon further treated as stated in Example 1. By extraction of the bicarbonate-alkaline solution with ether or benzol the vanillin bromide will be isolated and discharged upon volatilization of the solvent in the form of beautiful crystals. The yield is 70 g, that is 7 percent of the used lignin bromide.

Example 6

1 liter of commercial sulphite cellulose lye (corresponding to 40 g of lignin) is mixed with 300 g of caustic potash, the solution (boiling at 108°C) heated for 12 hours under reflux and at the same time oxygen passed therethrough. The reaction mixture is thereupon treated with carbonic acid and further worked-up as stated in Example 1. The yield amounts to 5 g of vanillin, that is 12.5 percent of the lignin contained in the waste-lye.

Example 7

1 liter of commercial sulphite cellulose waste-lye is brought to double alkalinity and mixed with common salt until saturation takes place. The solution having now its boiling point at 108°C is heated for 12 hours under reflux and at the same time oxygen is introduced in fine distribution; upon cooling this solution is further worked-up in the usual manner as stated in Example 1. The yield of vanillin is 4 to 5 g, that is 11 to 12 percent of the lignin contained in the sulphite cellulose lye.

The dependence of the yield from the action of the oxygen and from the boiling temperature is shown very instructively in the below Table giving the yields of vanillin for each liter of sulphite cellulose waste-lye obtained by treatment with and without oxygen as well as at several boiling temperatures (by adding different amounts of salt) but under otherwise exactly like conditions. These tests have been conducted without addition of an oxygen transmitting substance.

TABLE

Gas	Boiling temperature	Yield from 1 liter waste-lye	
		Vanillin	Lignin
	$^\circ \text{C}$.	Grams	Per cent
Nitrogen	101	0.2	0.5
Oxygen	101	3	7.5
Do	104	3.6	9.0
Do	107-108	4.5	11.25

Example 8

A comparison of the processes hitherto in use (for instance according to U. S. Patent 2,069,185) with our new process (which is conducted in two steps, that is by preliminarily boiling with alkali) may be obtained in the following manner:

4 liters of sulphite cellulose waste-lye (which corresponds to 160 g of lignin) are mixed with 480 g NaOH and heated for two hours and one half to 160° . The solution is thereupon divided into two halves.

The one half corresponding to 2 liters of sulphite waste-lye, or 110 g of lignin, is worked-up in the usual manner which yields 4 g of pure vanillin, that is 4 percent of the lignin contained in the sulphite waste-lye.

The other half is boiled for 12 hours under agitation and with introduction of oxygen at the reflux cooler with the cobalt hydroxide freshly prepared from 300 g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ by precipitation with NaOH and hydrogen peroxide. The working is carried out in the same manner as according to the above given Examples. There will be obtained from 8 to 9 g of pure vanillin which corresponds to a yield of 8 to 9 percent (figured with respect to the contents of lignin in the waste-lye). The yield obtained when working according to our invention, therefore, amounts to more than twice the yield obtainable with former processes.

Example 9

1 kg of lignin (produced from wood-flour in known manner by means of copper oxide ammonia (cuproxam) or muriatic acid is heated with 20 liters of 2n-alkaline lye for one hour in a closed container to 165° . Upon cooling the solution is mixed with 3 kg of potassium ferri-cyanide and the mixture heated 3 hours to 110° . Working-up the reaction product in the above indicated manner yields 50 g of vanillin, that is 5 percent of the original material.

Example 10

2 kg of wood-flour are stirred-up in an autoclave with agitator in 20 liters of a 10% potash lye and thoroughly mixed with 100 g of active carbon (Merck). Thereupon oxygen is pressed-in and the mixture is heated for about two hours under agitation to 120° . Upon cooling the solution is separated from undissolved matter and the vanillin isolated therefrom by extraction subsequent to treatment with mineral acid or carbonic acid according to the above given statements (see for instance Example 4). There are obtained 50 g of pure vanillin, that is a yield of 10 percent of the weight of the wood.

Example 11

1 kg of finely ground wood-flour is thoroughly mixed with 10 liters of alkaline lye of double normal value in an autoclave with agitator, thereupon oxygen is pressed in (at about 10 atmospheres over-pressure) and the mixture heated for two hours under thorough agitation to 120° . Now separation from the undissolved residue is effected and carbonic acid introduced into the solution until the whole of the caustic potash is converted into bicarbonate, whereupon the vanillin is withdrawn from the reaction mixture by extraction (with benzol or ether). Upon evaporation of the solvent there will be obtained 28.5 g of raw vanillin containing approximately 85 percent of pure vanillin yielding by re-crystallisation 24 g of pure vanillin, that is 9.6 percent figured with respect to the amount of lignin (250 g) present in the original wood-flour.

Example 12

50 g of "cuproxam lignin" produced from wood-flour or the like by extraction and treatment with copper oxide and ammonia are stirred-up in 2 liters of 2n-lye, mixed with 100 ccm nitro-benzol and boiled under extensive agitation and reflux for 72 hours. Upon removal of the nitro-benzol and its reduction products (at last with ether) the alkaline solution is acidulated, neutralized with bicarbonate and de-etherized. Upon evaporation of the ether there remains a yield of 6.25 g of a 90% raw vanillin corresponding to 12.5 percent of the used lignin. The degree of purity may suitably be ascertained with m-nitrobenz-hydracide. From the acidulated bicarbonate solution further oxidation products, such as vanillin acid, may be produced in small quantities.

Example 13

The same mixture of lignin, lye and nitro-benzol as given in Example 1 is heated in an autoclave with agitator. The working-up of the materials is likewise the same as according to Example 1. After heating for twenty hours to 160° the yield of raw vanillin amounted to 22 percent of the original material. Raising the temperature to 180° does not result in an increased yield. However, if heating is carried on to only 140° (same time) the yield will be smaller (18 percent).

Example 14

The same mixture of lignin and alkali as given in Examples 1 and 2 is heated with 100 ccm of nitrotoluol for 10 hours to 160° in an autoclave with agitator and further treated in the manner

above stated. The yield was 12 percent raw vanillin.

Example 15

40 g of dry pine-wood flour (corresponding approximately to 12 g of lignin) are treated for 20 hours in an autoclave with agitator with 400 ccm of 2n-lye and 50 ccm nitrobenzol at 160° which yields 1.5 g of raw vanillin corresponding to 12.5 percent of the used lignin.

Example 16

400 ccm of commercial sulphite cellulose waste-lye corresponding to 22 g of lignin are brought to alkalinity of double normal value by addition of solid alkali, thereupon mixed with 50 ccm of nitro-benzol and treated in an autoclave with agitator for 6 hours at 150°. Upon working-up in the above indicated manner there will be obtained approximately 4 g of raw vanillin corresponding to 18 percent of the used lignin.

Example 17

100 g of lignin residues (11 percent methoxyl content) originating from a wood saccharification process are treated as above indicated in an autoclave with agitator for 3 hours together with alkali and nitro-benzol at 160° and worked-up as above stated. There are obtained 8 to 9 g of raw vanillin corresponding to about 12 percent of the lignin contained in the raw material.

The amount of the used aromatic nitro-compound may be considerably reduced especially in case of greater treated quantities.

KARL FREUDENBERG.

WILLY LAUTSCH.

HANS BRENEK.

ALIEN PROPERTY CUSTODIAN

PRODUCTS

Willy O. Herrmann, Deisenhofen, and Wolfram Haehnel, Munich, Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 27, 1940

This invention relates to organic compounds, and more particularly to synthetic resins.

Aldehyde resins may be obtained by the condensation of aldehydes, frequently with an alkaline catalyst. See Ellis—The Chemistry of Synthetic Resins—Chapter 23.

This invention has as an object the preparation of modified aldehyde resins. A further object is the preparation of improved aldehyde resins. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein an aldehyde resin containing water of constitution has a portion or all of the water replaced by molecules of an organic or inorganic acid, alcohol, halogen, or other exchangeable compound alone or mixed.

The resins which may be produced from aldehydes such as acetaldehyde, crotonaldehyde, etc., particularly the solid, amorphous masses formed by thermal treatment, e. g., according to DRP-381,720, can, by reaction with chemical reagents, be converted in a surprising manner into new type compounds. The aldehyde resins are derivatives of acetylene and, in combination with the polyethine nuclei resulting from the condensation of the acetylene, they contain chemically combined water in different ratios. The new process deals with the partial or complete replacement of this water. The derivatives formed by this conversion may be considered as polyethine compounds of the composition $(C_2H_2)_x.K_y$, where K is an organic acid, inorganic acid, alcohol, halogen, or other exchangeable compound alone or mixed, and y may vary from 0 to x. K may also include water, but not alone, i. e., it is present along with an alcohol, acid, etc., which has but partially replaced it in the original aldehyde resin.

The following examples which are illustrative and not limitative exemplify the invention with respect to the preferred aldehyde resin "Wacker Artificial Shellac KR" obtained by a thermal hardening with or without alkalies of resins from acetaldehyde and its polymerization and condensation products according to German Patent 381,720. The elementary analysis of this resin is carbon 68.50%, hydrogen 8.26%.

Example I

100 g. of resin KR were dissolved in about 500 g. of hot glycerol and to the hot solution about 1/2 cc. of concentrated sulfuric acid was added in drops, the mixture being agitated. When the sulfuric acid was added, local reactions were set up with the formation of black lumps. On the next

day the contents of the flask had become almost solid and only a small amount of liquid remained. Water was added to the reaction product and boiled. By repeated washing or boiling with water, after drying on a clay plate in the open and in the drying oven at 120° C, 86 g. of a coffee brown powder were obtained. Its composition is carbon 72.04%, hydrogen 7.55%.

The product is partially soluble in alcohol and then gives a brittle brown resin melting at 120° C. The alcohol-insoluble portion is rather resistant to solvents and is amorphous.

Example II

10 g. of resin KR were dissolved in 70 cc. of glycol by heating. By the addition of several drops of sulfuric acid to the hot solution reaction took place with the formation of a dark precipitate. On another day the reaction product was covered with water, ground, boiled until the wash water was clear and, after drying at 120° C, gave about 7 g. of fawn-colored powder. Analysis gave carbon 71.11%, hydrogen 6.82%.

The product is partially soluble in alcohol and then gives a brown fusible resin. The alcohol-insoluble, amorphous portion is only partially soluble in other customary solvents such as acetone, benzene, etc.

Example III

10 g. of resin KR were dissolved in 60 cc. of hot formic acid and to this hot solution 4–5 drops of concentrated sulfuric acid were added. On the addition of sulfuric acid to the hot solution a mild reaction took place. After warming for 3 hours a dark resin was precipitated from the black solution by the addition of 200 cc. of water. This precipitate was washed with hot water and dried. The yield was 8.4 g. Analysis gave carbon 70.73%, hydrogen 7.17%. The saponification number was 442 to 465.

The product is originally blackish but by repeated boiling with water becomes fawn-colored. It is partially soluble in alcohol. The alcohol-soluble portion is a brittle brown resin with good solubility in the customary organic solvents. In methanol, tetrachloroethane, it is only partially soluble, in benzene it is only soluble in traces. The alcohol-insoluble portion is amorphous and difficultly soluble. In acetic acid, Methylanon, Palatinol M, and pyridine it dissolves partially when heated.

Example IV

30 g. of resin KR were dissolved in 150 cc. hot glacial acetic acid. To the cooled solution a mix-

ture of 2 cc. concentrated sulfuric acid in 50 cc. glacial acetic acid was added. When the sulfuric acid solution was added to the cooled mixture no visible reaction occurred, except for the development of a dark color. A vigorous reaction did not take place until the mixture was heated. The reaction mixture was held for several hours at the boiling point of acetic acid and the hot solution, solidifying below 100° C, was poured into water, whereby a blackish brown hard powder precipitated. By boiling with water and drying a coffee-brown powder, which swelled strongly in water, was obtained. The yield was approximately 25 g.

The product is partially alcohol-soluble. On combustion, the alcohol-soluble portion gave carbon 73.34%, hydrogen 6.74%, and a saponification number of 246.

In the case of the alcohol-insoluble portion, combustion gave carbon 72.76% and hydrogen 7.10%, and a saponification number of 213.

A polyethine acetate of the formula



has the composition: carbon 73.1%, hydrogen 7.3%.

Example V

50 g. of resin KR were dissolved in 250 cc. of glacial acetic acid and to the hot solution a mixture of 5 cc. concentrated sulfuric acid in 150 cc. glacial acetic acid was added. The reaction mixture was heated for 3 hours at the boiling point of the glacial acetic acid and then the distillable portion was distilled from the reaction flask on an oil bath. In the acetic acid which was driven off about 12 g. of saponifiable ester were determined. The solid reaction product, after washing with water and drying, gave a blackish brown, hard powder.

The yield was 46 g. Combustion gave carbon 73.98%, hydrogen 7.24%, and a saponification number of 257.

However, in comparison with the reaction product obtained according to Example IV, this product is less soluble. Both hot and cold it is only soluble in traces in benzene, butyl acetate, Methylanon, and tetrachloroethane.

Example VI

50 g. of resin KR were dissolved in 200 cc. of glacial acetic acid and then a mixture of 2 cc. concentrated sulfuric acid and 100 cc. of glacial acetic acid was introduced into the middle of the resin solution. This reaction mixture was boiled for 4 hours and the resulting dark solution poured into alcohol. Overnight a dark sludge separated, which was boiled several times with alcohol, and after drying at 120° C produced a fawn-brown powder.

On combustion this product gave carbon 73.24%, hydrogen 7.36% and had a saponification number of 316. Its composition corresponded, therefore, very well with the formula for a polyethine acetate as given in Example IV.

The alcohol-containing filtrate was concentrated on a water bath and poured into water. After drying the powder separating out gave a fawn-brown powder of the composition: carbon 70.97%, hydrogen 7.11% and had a saponification number of 297.

Example VII

10 g. of resin KR were dissolved in 50 cc. of hot glacial acetic acid and to the hot solution several drops of concentrated sulfuric acid were

added, a short vigorous reaction takes place at once accompanied by a darkening of the mixture. The solution was allowed to stand overnight and by the addition of 150 cc. of water a voluminous black compound was precipitated. By repeated washing with water and drying at 120° C about 8 g. of a brown product were obtained. This product was particularly voluminous in comparison with the other acetates produced according to Examples IV-VI.

Analysis gave carbon 70.67%, hydrogen 7.03%, and a saponification number of 263.

This product is very easily soluble. Cold it is partially soluble in acetone, benzene, butyl acetate, chloroform, acetic acid, methanol, Methylanon, Palatinol M, alcohol, tetrachloroethane; cold it is soluble in glycol only in traces also carbon tetrachloride, on the other hand it is almost soluble in pyridine when cold.

Hot it is completely soluble in Methylanon, Palatinol M, pyridine, tetrachloroethane; it is almost completely soluble in acetic acid.

By way of comparison the solubility characteristics of the product, obtained according to Example IV, are different. This product, both hot and cold, is for the most part only partially soluble in the solvents cited; in methanol it is only soluble in traces.

The product obtained according to Example VI is even less soluble. Both hot and cold it is insoluble in acetone, benzene, oil of turpentine, and vinyl acetate; hot and cold it is somewhat soluble in chloronaphthalene, chloroform, dichloroethylene, Palatinol C & M, and trichloroethylene; otherwise it is only soluble in traces.

The product obtained according to Example V is the least soluble. Both hot and cold it is only soluble in traces in benzene, butyl acetate, Methylanon, and tetrachloroethane; otherwise it is insoluble when cold.

Examples IV, V, VI, and VII show how the reaction with acetic acid may be modified in order to bring out the fact that products with different physical properties may be obtained to a large degree, e. g., products which are highly soluble or which are of low solubility, products which are in an easily pulverizable or are in a hard form, voluminous products or more compact products, products which are resinous and fusible or which are infusible and amorphous, different colored products, e. g., so that these products have a wide application in the fields where resins and other plastics are customarily used.

Example VIII

50 g. of resin KR are dissolved in 450 g. of glacial acetic acid. At room temperature chlorine is introduced into this solution. The solution, which originally had the characteristic red-yellow color of aldehyde resins, became light brown after an initial dark coloration. After the solution had taken up 56 g. of chlorine in 340 minutes, the reaction product was precipitated with 3 liters of water and washed with 9 more liters of water until it was chlorine and acid free. The reaction product was an almost white powder which contained 46.17% carbon, 4.8% hydrogen, and 34.37% chlorine. The yield was 88 g.

The chlorination product is very easily soluble in almost all organic solvents, e.g., acetone, butyl acetate, monochlorobenzene, benzene, chloroform, acetic acid, pyridine, and trichloroethylene.

The process and the form of the product obtained may be varied by the choice of different solvents, different halogens, by the addition of

halogen carriers, and also by varying the solvent, temperature, etc. of the chlorinating agent used. Therefore, another example of the chlorination may be given below.

Example IX

50 g. of resin KR were dissolved in 450 g. of glacial acetic acid. After the addition of 7.5 g. of phosphorous pentachloride, chlorine was led in while cooling the mixture to 0°C until there was an 80 g. increase in weight. By irradiation of the solution the reaction of the chlorine saturated solution could be so conducted that a light reaction product was obtained, which after isolation had a saponification number of 558. By precipitation of the mother liquor with methanol, a second almost white reaction product with a saponification number of 573 was isolated. A third white reaction product with a saponification number of 721 was obtained by the addition of water to the mother liquor.

Similar compounds may be obtained with other halogens. If bromine, dissolved in glacial acetic acid, is reacted on a solution of resin KR in acetic acid a black, bromine-containing product is obtained. By the action of iodine dissolved in a solution of acetic acid and alcohol, a blackish gray green, iodine-containing pulverulent product is precipitated from an acetic acid solution of resin KR.

While certain alcohols, acids, etc. have been exemplified above, the process of the present in-

vention is generically applicable to the replacement of at least a portion of the combined water of an aldehyde resin by alcohols, organic acids and halogens. Lower fatty acids, i.e., those up to four carbon atoms are a preferred class and of these acetic acid is particularly useful. Lower polyhydric alcohols, i.e., those having up to four carbon atoms are also useful. Monohydric alcohols may also be used. When an organic hydroxyl compound, e.g., a fatty acid or polyhydric alcohol is to replace the combined water in whole or in part, a catalyst, e.g., sulfuric acid, is particularly desirable.

The invention is exemplified above with KR resin, i.e., a thermo hardened acetaldehyde resin, but the process of the invention is applicable to any aldehyde resin, i.e., the resinification product of an aldehyde or mixture of aldehydes.

By the present process a new method is disclosed for obtaining new organic compounds particularly polyethine compounds. Their field of use is the same as that of previously known plastics, particularly the fields in which resins and polyvinyl compounds are used.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

WILLY O. HERRMANN,
WOLFRAM HAEHNEL.



356,289

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PROCESS FOR THE PURIFICATION OF PHOSPHATIDES

Aage Christiansen, Russhov, near Aarhus, Den-
mark; vested in the Alien Property Custodian

No Drawing. Application filed March 6, 1940

The present invention relates to a process for purification of phosphatides separated from vegetable oils.

The raw phosphatide that may be gained from vegetable oils by precipitation with suitable quantities of water, maybe with chemicals added, consists of an emulsified more or less paste-like mass containing, besides phosphatide and water and possibly chemicals also oil and impurities the removal of which is necessary for using the phosphatide, and which oil and impurities cannot be separated by treatment in a centrifugal, nor by other mechanical methods, but require the addition of chemical means, in order to be removed.

In order to purify such raw phosphatide, it has therefore been proposed partly to extract with oil-dissolving agents and partly to wash with such substances as ethyl alcohol, methyl alcohol, acetone and the like, i.e. with cleaning agents that are more or less soluble in oil as well as in water, and when added in suitable large quantities, will precipitate the phosphatides, which then are cleaned more thoroughly by a repeated treatment with the cleaning agent.

These purifying methods, however, require the use of relatively large quantities of the purifying agents concerned, frequently several times the quantity by weight of the phosphatide, for which reason the processes become complicated and expensive, while for economical reasons a recuperation of the cleaning agent is required. In the Danish Patent No. 52738 a method is described according to which, besides large quantities of alcohol, also considerable quantities of water are added, especially with the simultaneous use of various acids and salts. In this case the quantities to be treated will be especially large per se, and the process becomes complicated, in that the mixture divides itself into three layers of which the one mainly contains phosphatides, another one oil, while a third one contains phosphatides in such a quantity that it has to be treated again, in order that the contents of phosphatides may be gained. These methods are further lengthy and involve a danger of the easily decomposable phosphatide becoming destructed.

Experience has now shown that after the addition of relatively small quantities of one or more of the said cleaning agents, such as alcohols and ketones that are more or less soluble in water as well as in oil, precipitated watery raw phosphatides may be caused to melt, maybe after being heated.

The fused mass may be separated, either by being left alone or by being treated at a suitable

temperature in a centrifugal, and gives then only two layers:

1. An oil-containing layer containing a small part of the added cleaning agent and being more or less coloured and mixed with the impurities desired to be removed,

2. A liquid purified layer of phosphatides containing practically all the pure phosphatides present in the raw phosphatides.

The quantity of cleaning agent to be added, in order to cause the watery phosphatide mass to pass into a liquid state must be adjusted according to the nature and conditions of manufacture of the raw phosphatide, and may vary from 1 to 33% of the cleaning agent, figured relatively to the contents of raw phosphatide. If too little of the cleaning agent be used, no useful separation will be effected, and if more than the optimum quantity of the agent be used, a coagulation will take place, and after the mixture has been left alone or has been treated in a centrifugal, the result will be an incomplete purification and a separation into three layers:

At the top: an oil-containing layer,
Midways: water, plus cleaning agent plus a small quantity of phosphatide,

At the bottom: an imperfectly purified mass of phosphatide.

The layer of phosphatide (layer 2) purified according to the present process may either be dried as it is, or it may be further cleaned by being mixed with oils or fatty substances, and owing to the presence of the cleaning agent, the oil and fat may again be separated together with the absorbed impurities by being left alone or by being treated in a centrifugal, maybe under heating.

This combination of the cleaning agent and oil causes the added oil to absorb especially colouring substances, fatty acids, tasting substances and other impurities from the phosphatides and further the quantity of phosphatide may be practically completely gained.

Example 1

To the ground-nut raw phosphatide, separated from raw ground-nut oil by means of water and containing about 40% of pure phosphatide, about 10% of ethyl alcohol is added, and is mixed while heating to 60 to 70°C causing the mass to melt, after which it is separated, by being left alone or by treatment in a centrifugal, into:

1. A lighter oil-containing layer containing impurities and a small quantity of alcohol and

2. A heavier liquid layer consisting of purified phosphatide, some water and the main part of the alcohol added.

After the separation, this layer is mixed with 33% of refined vegetable oil, and the mixture is heated to from 60 to 70° C., after which it is separated by being left alone or by treatment in a centrifugal into:

1. An oil-containing layer in which the impurities and a small quantity of alcohol have been absorbed, and

2. A liquid layer containing, besides water and alcohol, also a more thoroughly purified phosphatide.

AAGE CHRISTIANSEN.

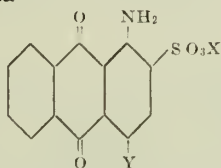
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CONDENSATION PRODUCTS OF THE
ANTHRAQUINONE SERIES

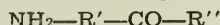
Winfred Hentrich, Dessau-Rosslau, and Heinz-Joachim Engelbrecht, Dessau, Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 6, 1940

It has been found that new condensation-products of the anthraquinone series are obtainable by condensing 4-halogen-1-amino-anthraquinone-2-sulfonic acid or its alkali salts of the general formula



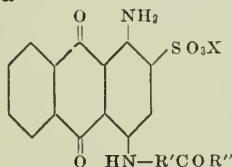
wherein X stands for hydrogen or for an alkali metal atom and Y for a halogen of the group chlorine, bromine and iodine, with amino-aryl-alkyl-ketones of the following formula



wherein R' represents a radical of the benzene series which may be halogenated, hydroxylated or alkylated and contain the NH₂-group in the radical R' in meta-position, and R'' stands for an alkyl residue which may still be halogenated or hydroxylated. The condensation is effected by heating up the components in the presence of water, an acid-binding agent such as sodium-carbonate and a little amount of a copper-compound e. g. cuprous chloride.

The same products are likewise obtained by the condensing of an amino-aryl-alkyl-ketone with a 1-amino-2,4-dihalogen-anthraquinone and by the exchanging of the halogen atom in the 1-amino-2-halogen-4-aryldio-anthraquinone obtainable by condensation as above indicated, for a sulfonic acid group and preferably by a treatment with an alkali metal sulfite.

The new products are characterized by the following formula



wherein X stands for hydrogen or for an alkali metal atom, whereas R' represents a radical of the benzene series in which the NH-group stands in meta-position, and R'' an alkyl residue. The new products are dyestuffs which dye wool and silk from an acid bath blue tints of very good fastness-properties. Moreover the new dyestuffs are of an excellent equalizing-power.

The following examples serve to illustrate the new invention but they are not intended to limit it thereto:

Example 1

101 parts by weight of 4-bromo-1-amino-anthraquinone-2-sulfonic acid sodium, 35 parts by weight of 3-amino-acetophenone, 20 of anhydrous sodium carbonate and 5 of cuprous chloride are heated up to 75–85°C together with 600 parts by weight of water while well stirring and gradually raising the temperature. We maintain this temperature until the formation of dyestuff is finished. The working-up and purifying of the dyestuff is done to usual methods. The thus obtained dyestuff is a blue crystalline powder dyeing wool and silk from an acid bath pure blue tints.

Instead of 3-amino-aceto-phenone we may likewise use 3-amino-propio-phenone, 3-amino-butyro-phenone, 2,4,6-tribromo-3-amino-aceto-phenone and 5-amino-2,4-dimethyl-aceto-phenone.

Example 2

76 parts by weight of 2,4-dibromo-1-amino-anthraquinone, 30 parts by weight of 3-amino-acetophenone, 40 of anhydrous potassium-acetate, 1.0 parts by weight of copper-acetate, 1.0 of copper-bronze are heated in the autoclave for 18 hours up to about 150 to 160°C in 750 parts by volume of amyl-alcohol while stirring. After cooling the isolated condensation-product is sucked off, then washed with alcohol and water and finally dried.

For the converting into the sulfonic acid 44 parts by weight of the condensation-product are heated at the reflux cooler up to a gentle boiling, together with 180 parts by weight of phenol, 40 of potassium sulfite and 100 of water, until the dyestuff becomes soluble in water. After removing the phenol by steam-distilling the reaction-mixture is filtered whereupon the thus formed dyestuff is separated from the filtrate in the usual manner.

Example 3

40 parts by weight of 4-bromo-1-amino-anthraquinone-2-sulfonic sodium, 18 parts of 3-amino-butyro-phenone, 8 of anhydrous sodium carbonate and 2 of cuprous chloride are heated together with 250 parts by weight of water while stirring and gradually warming up to 80–100°C. We maintain this temperature until the formation of dyestuff is finished, whereupon the dyestuff is worked up in the usual way. The isolated dyestuff dyes wool and silk from an acid bath beautiful blue tints.

WINFRID HENTRICH.
HEINZ-JOACHIM ENGELBRECHT.

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ALIEN PROPERTY CUSTODIAN

PROCESS FOR TREATING NAPHTHENIC HYDROCARBON DISTILLATES

Adrianus Johannes van Peski, Amsterdam, The
Netherlands; vested in the Alien Property Cus-
todian

No Drawing. Application filed March 11, 1940

The present invention relates to a process for treating naphthenic hydrocarbon distillates and particularly such distillates as comprise appreciable concentrations of naphthene hydrocarbons in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C.

In the production of certain premium fuels and in certain processes employing naphthenic crude oils, hydrocarbon distillates containing substantial proportions of naphthenic hydrocarbons in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C. are obtained. These fractions are not of great value per se and have hitherto usually been subjected to a dehydrogenation treatment to convert the naphthenic hydrocarbons to aromatic hydrocarbons. The aromatic fractions thus produced, however, generally have a low lead susceptibility and are now falling into disfavor. I have found that these various naphthenic distillates may generally be considerably improved by subjecting them to a suitable treatment to selectively isomerize certain naphthenic hydrocarbons therein. In order to obtain the desired improvements it is necessary, however, to avoid as far as possible the degradation of the paraffinic hydrocarbons and the various condensation and alkylation reactions which tend to take place to form undesirable high molecular weight hydrocarbons.

It is known that butane, and to a certain extent pentane, may be isomerized with the aid of aluminum halide catalysts provided that the concentration of the aluminum halide is kept sufficiently low, and only small amounts of hydrogen halides are present. The higher paraffin hydrocarbons, such as those containing six or more carbon atoms, on the other hand, cannot be economically isomerized to any appreciable extent under the employed conditions without excessive degradation. Therefore, although it has long been known that certain of the lower simple naphthenic hydrocarbons per se could be isomerized with the aid of acid-acting metal halide isomerization catalysts, it was to be expected that the treatment of these hydrocarbons when in admixture with higher paraffinic hydrocarbons in commercial distillates with isomerization catalysts would lead primarily to degradation reactions, condensation reactions and the like, and that isomerization of the naphthenic hydrocarbons would not take place to any appreciable extent. As a matter of fact, it is known that under the usual isomerizing conditions the presence of

naphthenic hydrocarbons tends to increase the already great tendency of higher paraffinic hydrocarbons to decompose under the influence of aluminum chloride. Thus, one of the foremost authorities on aluminum chloride catalysis states in U. S. Patent No. 2,083,598, "It has been observed that if paraffinic hydrocarbons are heated alone in the presence of aluminum chloride only a very limited amount of decomposition occurs while, if ring hydrocarbons are present, to act as acceptors, extensive decomposition of the paraffins is evidenced from the formation of large quantities of alkylated ring compounds." By treating mixtures of naphthenic hydrocarbons and paraffinic hydrocarbons with aluminum chloride and hydrogen chloride at temperatures in the neighborhood of 175°C., a large amount of degradation of the paraffinic hydrocarbons occurs and a product having a wide boiling range and consisting of lower paraffinic hydrocarbons and higher boiling alkylated naphthenic hydrocarbons is produced.

I have found that although naphthenic hydrocarbons when in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C. tend to promote the degradation of the paraffinic hydrocarbons by acid-acting metal halide isomerization catalysts, such as aluminum chloride, this is only the case at temperatures ranging from about 150°C. to about 200°C. and above. At temperatures below about 150°C., usually between about 40 and about 130°C., I have found that the effect of naphthenic hydrocarbons in such mixtures is exactly opposite to that expected. Under suitable conditions and at these temperatures, the naphthenic hydrocarbons tend, I have found, to inhibit the normal decomposition of paraffinic hydrocarbons by aluminum chloride and to undergo a clean-cut isomerization. Thus, contrary to expectation, it is actually possible to effect a selective isomerization of the naphthenic hydrocarbons when in admixture with higher paraffinic hydrocarbons under conditions where the higher paraffinic hydrocarbons alone would normally undergo substantial degradation.

The process of my invention may be applied to improve any hydrocarbon distillate containing an appreciable concentration of naphthenic hydrocarbons in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C. It is particularly suited and advantageous for the treatment of such of these stocks as boil predominantly between about 40°C. and 205°C., and becomes increasingly advanta-

geous as the ratio of naphthenic hydrocarbons to higher paraffinic hydrocarbons increases. Thus the process may be advantageously employed with stocks containing as low as about 5-10% naphthenic hydrocarbons, but is much more advantageous when the naphthenic hydrocarbon concentration is at least 20% or higher, for instance 70%. This appears to be due to the greater inhibition of degradation of the higher paraffinic hydrocarbons exerted by the higher concentrations of naphthenic hydrocarbons. Also, although the process is advantageous and may be employed to treat hydrocarbon stocks containing relatively high molecular weight hydrocarbons having normal boiling points in the neighborhood of 150 to 250°C., it is most advantageous and is preferably employed with such distillates as have a substantial content of hydrocarbons boiling in the range of from about 67-150°C. The reason for this is that the most important advantage realized when treating naphthenic distillates according to the process is due to the isomerization of certain naphthenic hydrocarbons boiling in this range. Particular naphthenic hydrocarbons which may undergo isomerization in the process are for example, cyclopentane, the various alkylated cyclopentanes, cyclohexane, the various alkylated cyclohexanes, and cycloheptane and its various alkylated derivatives.

In order to obtain the best results using the present process, it is preferable that the stock treated be substantially free of olefines. The reason for this is that olefins, if present in substantial quantities, tend to polymerize and undergo various other reactions which are, in general, detrimental. Aromatic hydrocarbons also, if present in appreciable quantities (for example about 12% or above), or undesirable since they tend to react with the naphthenic hydrocarbons under the reaction conditions to form high boiling products of little value. If the stock to be treated contains substantial quantities of olefinic or aromatic hydrocarbons these may be first removed or reduced to unobjectionable concentrations by a suitable treatment, such, for instance, as selective solvent extraction, hydrogenation, etc. Any other minor impurities in the distillate to be treated which are known to be detrimental to the activity of aluminum chloride and other acid-acting metal halide isomerization catalysts, may be removed, if present, by a conventional hydrogenation or refining treatment.

The various naphthenic stocks are treated, according to the present invention, by contacting them at a suitable temperature in the liquid phase, and in the presence of a hydrogen halide with an acid-acting metal halide isomerization catalyst. Of the various applicable acid-acting metal halide isomerization catalysts, anhydrous aluminum chloride is by far the most efficient and preferred. Other acid-acting metal halide isomerization catalysts, such as the halides of Zr, Zn, Sn, Be, Nb, Ta, Sb, B, Co, Ni, Cu, and Cd may also be employed, if desired in conjunction with aluminum chloride. The anhydrous aluminum chloride, if this catalyst is used, may be employed in a number of ways. One suitable method of employing this catalyst is to suspend the finely-divided aluminum chloride in the reaction mixture; for this method of operation the reactor system described in copending application (Ser. No. 298,594 filed October 9, 1939) may be advantageously employed. Another method of applying aluminum chloride is as complex double compounds of the type known as the "Gustavson

Compounds." Still another advantageous way to employ aluminum chloride is to apply it to an adsorptive carrier material and pass the hydrocarbon thereover.

The catalyst may be employed in any amount ranging from about 1% to about 25%, depending upon the stock treated, the activity of catalyst, the amount of hydrogen halide present, and the temperature. In general, the effectiveness of the catalyst under any given set of conditions is a linear function of the concentration up to a concentration at which degradation is promoted. If, therefore, under any given set of conditions excessive degradation tends to take place, this may usually be remedied, if the temperature is not too high, by decreasing the concentration of catalyst.

In order to avoid substantial degradation of the higher paraffinic hydrocarbons and the production of undesirable higher alkylated naphthenic hydrocarbons, it is essential that the process be executed at a temperature not higher than about 150°C. and at the very most 150°C. In general, the most applicable temperatures are from about 60-130°C. Since the rates of the desired reactions increase rapidly with the temperature up to the point where substantial degradation and alkylation begin, it is advantageous to adjust the temperature to just below that at which substantial degradation begins. The reaction can, however, be executed, if desired, at lower temperatures, but requires longer contact times (which are not generally practical) to obtain an appreciable improvement; for example, if a naphthenic hydrocarbon distillate containing less than about 5% of aromatic hydrocarbons is treated at 20°C., a contact time of from several hours to several days may be required, depending upon the feed, catalyst, etc.

The treatment, according to the present process, is always executed in the presence of at least a small amount of free hydrogen halide. Although small amounts of free hydrogen halide are sufficient to promote the desired reactions, I have found that much better results are obtained by employing larger amounts. Thus, for example, according to a preferred embodiment of my invention, the process is executed under a pressure of hydrogen halide at least equivalent to one atmosphere and preferably equivalent to at least three atmospheres when measured at 25°C.

The advantages realized by treating commercial naphthenic hydrocarbon distillates according to the present process are manifold and depend somewhat upon the use or treatment to which the treated stock is to be subsequently applied. Thus, suitable stocks may be treated according to the present process to improve their stability and ignition properties; they may be treated and fractionated with a view of obtaining various close fractions having a high concentration of a particular type of hydrocarbon or specific properties; or they may be treated with a view of rendering the stock more suitable for a subsequent treatment. For example, by treating naphthenic stocks according to the present process and then by a dehydrogenation treatment, much higher yields of aromatic hydrocarbon may generally be produced than with the same stock untreated.

In order to illustrate the process the following examples, showing results obtained with comparatively simple hydrocarbon mixtures, are presented. Other more complex mixtures and commercial naphthenic fractions of various compositions have also been treated successfully, and

it is therefore to be understood that the following examples are not to be considered as limiting the invention in any manner.

Example I

A hydrocarbon mixture consisting essentially of 80% by weight of normal heptane and 20% by weight methyl cyclopentane was treated with 5% by weight of anhydrous aluminum chloride and 5% by weight hydrogen chloride at about 100° C. for five hours. The product analyzed as follows:

	Per cent
Heptane	78.2
Cyclohexane	16.8
Methyl cyclopentane	5.0

Thus, under conditions where normal heptane itself would normally be predominantly decomposed, no appreciable degradation took place and the labile and thermally less stable methyl cyclopentane was approximately $\frac{3}{4}$ converted into the more desirable cyclohexane.

Example II

A naphthenic gasoline was fractionated and a fraction boiling between 65°C. and 75°C. collected. This fraction which consisted of about

	Per cent by weight
Naphthenic hydrocarbons	60
Aromatic hydrocarbons	10
Paraffinic hydrocarbons	30

was treated with 1% by weight of aluminum chloride and 5% by weight of HCl in an autoclave at 80°C. for ten hours.

After decantation from the $AlCl_3$ the product obtained was washed with lye and water and then dried. The reaction product was subsequently subjected to a sharp rectification, whereupon 45% by weight of a cyclohexane fraction boiling between 78 and 80.5°C., having a refractive index of 1.4265-20/0, was obtained.

Example III

750 grams of a Borneo gasoline fraction boiling between 85°C. and 104°C. and consisting approximately of

	Per cent
Naphthenic hydrocarbons	74
Aromatic hydrocarbons	3
Paraffinic hydrocarbons	23

was treated with 40 grams of anhydrous aluminum chloride, and 100 grams anhydrous HCl for ten hours at 80°C. in a 2 liter stirring autoclave. The product, after washing and drying, consisted approximately of

	Per cent
Naphthenic hydrocarbons	73
Aromatic hydrocarbons	2
Paraffinic hydrocarbons	25

This treated gasoline fraction, when subjected to a dehydrogenation treatment, was found to give much superior yields of aromatic hydrocarbons.

Example IV

A fraction of a straight-run gasoline from a Venezuelan crude boiling between 85°C. and 104°C., and consisting approximately of

	Per cent
Aromatic hydrocarbons	6
Hydroaromatic cycloparaffinic hydrocarbons ..	29
Non-hydroaromatic cycloparaffinic hydrocarbons ..	25
Paraffinic hydrocarbons	40

was treated as follows: 4% of anhydrous HCl was dissolved in the distillate and the mixture forced at a rate of 1 liter per hour under a pressure of about 15 atmospheres through a 2 liter stirring autoclave containing 500 grams of aluminum chloride and maintained at a temperature of 80°C. After treating about 140 liters, small quantities of aluminum chloride were intermittently added to the autoclave to maintain the catalytic activity. At the very beginning a portion of the small amount of aromatic hydrocarbons contained in the feed was consumed to produce a complex compound of the Gustavson type with the aluminum chloride. The product, after washing with caustic, washing with water, and drying, consisted approximately of

	Per cent
Aromatic hydrocarbons	6
Hydroaromatic cycloparaffinic hydrocarbons ..	46
Non-hydroaromatic cycloparaffinic hydrocarbons ..	8
Paraffinic hydrocarbons	40

Thus, it is seen that the content of non-hydroaromatic hydrocarbons was reduced from about 25% to about 8% while the concentration of valuable aromatic hydrocarbons was not appreciably altered and degradation of the paraffinic hydrocarbons was substantially avoided. This treated distillate is exceptionally suited for a conventional reforming treatment.

The present application is a continuation-in-part of my copending application, Serial No. 270,655 filed April 28, 1939.

While I have described my invention in its preferred embodiments and indicated certain variations thereof, these are not to be construed as limiting the invention. It is to be understood that no limitations other than those imposed by the scope of the appended claims are intended.

ADRIANUS JOHANNES VAN PESKI.

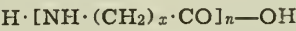
ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF HIGH
POLYMERIC COMPOUNDS

Max Hagedorn, Dessau, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed March 12, 1940

This invention relates to the production of high polymeric compounds. The superpolyamides known at the present time and used in the production of artificial filaments, fibers, foils etc., obtained from monobasic amino carboxylic acids by outer amide formation correspond to the formula



These polymers possess between the —NH— and the —CO— group in the practically utilizable form within the *n*-times recurring structure-unit at least 5 C-atoms and more. This corresponds in the formula above to an *x*=7 or 8. The superpolyamides hitherto known with structural units between the —NH— and the —CO— group of less than 6 C-atoms are brittle and of bad mechanical qualities, even though they contain this structural unit in the molecule to a certain percentage only.

According to this invention it has been found that mechanically valuable mixed superpolyamides, containing between the —NH— and the —CO— group in the structural unit 4 C-atoms and less, are obtained, if this short structural unit contains an aromatic radical. This aromatic radical may be introduced by aromatic substitution of the structural unit at any place, that means in the —NH— or —CH₂— group, or may be placed as member between the —NH— and —CO— group. Such mixed polymers, besides their better mechanical qualities, are more easily obtainable, because they are formed at lower temperature and in shorter time. They also show noteworthy qualities for the production of foils.

Besides their usefulness for textile purposes in the form of filaments they are well suited for the production of films (for photographic and other purposes), plates (as substitute for glass), sheets or foils (for electric insulation, coating foils for cigarette tips, wrapping foils, adhesive foils, light filters, patterns, stencils, supports for prints or the like), sound records (either those in which the sound track is cut mechanically into the support or is impressed therein without removal of material (the Edison or the Berliner method)), masses for the reproduction and printing arts, masses for die-casting and molding by pressure (production of camera parts and casings for rollfilms or filmpacks by pressing or rolling, production of spools or parts thereof for photographic rollfilms by the molding method), as adhesive or intermediate layers for composite glass. The sheets or foils made from the materials according to this invention may be pro-

vided with a metallic coating according to a known process.

It is therefore an object of the present invention to provide a process of producing high polymeric compounds by polymerisating *ω*-amino carboxylic acids with amino carboxylic acids containing an aromatic radical.

A further object is the provision of a process by which polymerisates can be obtained, which are capable of being worked up into fibers, films, sheets, foils and the like.

Another object is the provision of a polymerization process, which is carried out in the absence of oxygen.

An additional object resides in the provision of suitable polymerization catalysts.

Another object is the provision of a process in which the molten reaction product is heated up at a temperature above the reaction temperature, if necessary by a vacuum treatment.

A still further object is the provision of a continuous process for the production of said high polymeric compound.

A still further object of the invention resides in a process, in which the reaction takes place under a protective layer consisting of a molten indifferent material.

Other additional objects will become apparent as the description proceeds.

This invention is based on the observation that very valuable polymers of the kind referred to are obtained by inter-condensation or polymerization with *ω*-amino carboxylic acids possessing not more than 4 C-atoms and containing an aromatic radical. The amino carboxylic acids may be used in this form or in the form of their condensable derivatives like anhydrides, acid chlorides, lactams, esters. As to the amino carboxylic acids containing an aromatic radical, compounds are used like phenyl- and naphthylalanine, phenyl-amino acetic acid and tyrosine. The aromatic radical may be directly built in between the —NH— and —CO— group, for instance, as in the 3-aminobenzoic acid and in aromatic amino carboxylic acids of similar constitution.

The molar proportion between the components is widely variable, but preferably the amino carboxylic acids with a longer chain, that means the one not containing the aromatic radical, should prevail. As example for such amino carboxylic acids there is mentioned the *ω*-aminocaproic acid and its similar derivatives like the anhydride, the lactam, the acid amide, the acid halides and esters.

The reaction between the two different amino

carboxylic acids may be accomplished in different ways. The components may be melted together. Thereby an indifferent component, for instance paraffin of a melting point 40 to 80°C not being a solvent for one or both components, may be added in order to reduce the heat of reaction or to facilitate the separation of the water. It is also possible to choose the diluent so, that it is a solvent for the final product for instance, like aniline at higher temperature. This should be added, if desired, towards the end of the reaction. The components however may be caused to react on each other in an indifferent solvent like phenols of all kind. According to the nature and qualities of the reaction product such compounds are added, in which the high polymer is soluble or not soluble.

The reaction temperature lies practically between 175 and 250° C. At temperatures below 175° C the formation of high polymeric compounds in some cases also sets in, proceeding, however, very slowly and not leading to products with improved mechanical qualities. Decisive for the quality of high polymeric final products is the absolute purity of the starting material and the careful exclusion of oxygen during the reaction. One works best therefore in the atmosphere of an indifferent gas such as CO₂, N₂ etc. and care has to be taken during the manufacturing process to exclude oxygen at temperatures above 150° C. In most cases it is sufficient to carry out the reaction at normal atmospheric pressure. If one of the reaction components shows great tendency to sublime, this may be counter acted by application of pressure, which is also applicable in such cases, where the reaction of the different components represents a true polymerization without splitting off of water. If the reaction however takes place without separation of water, it is advisable to avoid the undesirable points of certain reaction equilibria by application of pressure in excess and to work at a certain vacuum. In such cases it is most convenient, as mentioned, to apply a dissolving or not dissolving medium, which enhances the removal of water by lowering the partial pressure of the water vapor. The reaction may be advantageously performed as a continuous operation.

According to the constitution of the reaction components it is often practical to accelerate the polymerization and condensation by adding a catalyst. Advantageously, the accelerating materials used, if desired in conjunction with water or hydroxyl or sulphhydryl compounds, are acids, bases or salts or substances or mixtures of substances which form these. Correspondingly, acceleration occurs already if a small portion of water or of a hydroxyl compound or of a mercaptan is added. Since these substances, at least when the operation is conducted in a closed vessel, react in part stoichiometrically or in part until a definite equilibrium is attained, their proportion must in most cases be exactly adjusted in order that good reproducible results may be obtained. This is especially the case with alcohols and mercaptans of high molecular weight. In the case of materials of lower molecular weight, an equilibrium may occur rather in the course of the heating, particularly in the final phase. In certain cases, for instance when phenols are used, a considerable excess may be employed. Instead of free acids, functional derivatives thereof may be used, insofar as they have a tendency to acylate reactive hydrogen, especially acid chlorides, also, however, freely reactive acid esters, for instance

phenol esters of carboxylic acids and acid amides.

Especially favourable have proved salts of amino compounds capable of acylation, particularly those having primary amino nitrogen. Salts of secondary amines are in general less advantageous, since they appear to accelerate also the elimination of ammonia. Of the salts of primary amines, those of the amino acids are of special interest, because they favour a very uniform course of reaction. Since the number of the finally present end-groups and therewith the degree of polymerization is associated with the proportion of the catalyst, this proportion will in general be kept within comparatively narrow limits, at least when production of very highly polymeric products is desired. In most cases, it has proved advantageous to keep during the main reaction period a proportion of the substance which determines the formation of the end-groups below 1/50 equivalent in relation to the reaction that forms the end-groups. It has been remarked, however, that in many cases one cannot ascertain with certainty what the amount of the added accelerator is in fact consumed for the formation of the end-groups. Occasionally, suitable substances for forming end-groups are so changed that they cannot be regenerated. In the case of aminosulphonic acids, for instance sulphanilic acid, it has been observed that the sulpho groups are eliminated.

When the promoting substance is decomposed in the course of heating without formation of stable end-groups, it volatilises or becomes chemically inactive and may obviously be added in a larger proportion; for example when mixtures of lactams and amino acid esters are heated or when vapour of ammonia or an amine of low molecular weight is passed through molten lactam or mixture of lactams at a suitably high temperature, if desired under pressure.

The nature of the final product may be influenced both by the chemical composition of the catalyst and also by the proportion and the mode in which it is added. When the accelerator used is one which is practically not decomposed and acts as a true catalyst, for instance an inorganic halide in the presence of a trace of water, large variations in the proportion may have no essential influence on the properties of the final product. The position is otherwise, however, as has already been indicated, when the accelerator or constituent thereof, for example the cationic portion of a salt, is decomposed during the reaction more or less profoundly for the formation of the end-groups or of substances producing the end-groups. In such cases the desired degree of polymerization may be controlled and predetermined by using the accelerator in doses within certain limits. This is an essential advantage of the process. Moreover, the substances forming the end-groups may be determined in dependence on the substituents present and also on their electro-chemical character.

The higher the degree of polymerization, the more must the capacity for binding acid and therewith the quantitative adsorption of acid dyestuffs by the polymerisate or by the structure formed therefrom diminish. This retrogression in affinity for dyestuffs may be counteracted if as the accelerator there are used compounds forming end-groups capable of forming such end-groups as may be acylated, which compounds, besides the groups capable of acylation and of reaction with the lactam, for instance hydroxyl or amino groups or both, contain basic groups

which are incapable or only feebly capable of being acylated. Such materials are, for example, unsymmetrical dimethylpropylenediamine, ω -piperidopentylamine, and others having more than one nitrogen atom listed in the aforesaid table. By suitable choice of the accelerator forming the end-groups the capacity of the structure as a wetting agent and for swelling may be influenced within certain limits.

Table

Substances which are applicable as accelerators of the reaction:

1. *Inorganic compounds.*—Hydrogen bromide (as aqueous acid having a specific gravity of 1.48), Mixture of sulphuric acid and water in proportion of 98:36, Ammoniumfluoride, lithium chloride, hydroxylaminohydrochloride, magnesium chloride, zinc chloride, borofluoridedihydrate, aluminium chloride and other catalysts for Friedel Crafts reactions, sodium amide, lithium hydroxide.

2. *Organic hydroxyl- and sulphhydryl compounds.*—Benzyl alcohol, ω -dimethylamino-para-ethylphenol, dodecylalcohol, cholestrin, thioglycolic acid dodecyl ester, iso-octylphenol and iso-octylphenol ethyl ether.

3. *Amines and salts of organic amino compounds.*—Benzylamine, octadecylamine, octamethylenediamine, guanidine carbonate, N-butylaminofluorosulphonate, dodecylaminohydrochloride, abietinylaminohydrochloride, 9-aminopentatriacontane hydrochloride, butanolamino hydrochloride, β -chloroethylaminohydrochloride, triethylenetetramine-tetrahydrochloride, $\beta\beta$ -diamino-diethylether-dihydrochloride, $\beta\beta$ -diaminodiethylsulphidedihydrochloride, anilinohydrochloride, benzidiure-dihydrochloride, para-aminothiophenolhydrochloride, pyridine-camphorsulphonate, histaminedihydrochloride, melaminehydrochloride, sarcosinehydrochloride, cyclohexane- α -aminocarboxylic acid hydrobromide, para-aminobenzoic acid hydrobromide, para-aminophenyl acid ester hydrochloride, aminoethanesulphonic acid, sulphanilic acid.

4. *Organic acids and acid derivatives.*—Toluenesulphonic acid, naphthalenesulphonic acid, meta-sulphobenzoic acid (these above preferably in the presence of small quantities of water, of mono- or polyvalent alcohols, phenols or mercaptans, for example of benzyl alcohol, phenoxyethyl alcohol, diethylene-glycol, hexamethylene-glycol, vinyloctadecyl ether), oxyethanesulphonic acid, adipic acid, terephthalic acid chloride, cyanuric chloride, 1:3:5-benzenetricarboxylic acid chloride, laurylcyanamide, toluenesulphonic acid ethyl ester in presence of very small quantities of water (1/200 mol ester + 1/200 mol water to 1 mol lactam).

5. *Salt-like organic compounds especially such as are of preponderant basic character.*—Carbazole potassium, aluminium ethylate, magnesium oleate, potassium acetate in combination with cyclohexanol or dodecylalcohol, sulphosalicylic acid sodium.

6. *Substances which react with formation of organic acids.*—Benzyl chloride, para-xylylene bromide, butylchloromethyl ether, especially in presence of small quantities of water, alcohols, phenols or mercaptans, which may be present in small excess as compared with the halogen compound.

One may omit, however, to add special catalysts especially when the longer reaction component is employed in the form of its lactam. Most

probably the other amino carboxylic acid, containing the aromatic radical proofs enough reaction accelerating.

The shorter reaction time is very characteristic for the formation of mixed polymers according to this invention, which in most cases does not exceed 6–9 hours and which therefore is much shorter than that for the superpolyamides hitherto known without containing aromatic radicals.

In using promoters forming end-groups, which have more than two reactive groups, for example hydrochlorides of tri- and polybasic amines, especially primary amines or acid chlorides of free or polybasic carboxylic and sulphonic acids, there may be produced three-dimensional products which are fusible and soluble and chemically not net-like, which for many purposes are of especial interest, since by the action of substances having in the molecule at least two amino- and/or carboxyl groups, as compared with groups functionally reactive with formation of covalent linking, may be hardened or tanned, thus diminishing its capacity for swelling and raising the melting point.

Suitable substances are polyfunctional compounds having alkylating and/or acylating groups; also reactive carbonyl compounds and functional derivatives thereof, for instance dicarboxylic acids and their derivatives, such as adipic acid, maleic acid anhydride, diphenylcarbonate, dimethyloxalate, cyanuric chloride, diisocyanates, for instance para-phenylene-diisocyanate, and such substances produced by heating, such as hexamethylene-bis-carbamic acid methyl ester, hexamethylene-bis-carbamic acid phenyl ester; compounds having both alkylating and acylating function, for instance methylchloracetate, methacrylate; polyvalent alkylating agents, for instance 1:4-dichlorobutene, epichlorhydrin, tetrachloroxypropylammonium chloride, butadiene-dioxide, butadiene-disulphide, $\alpha:\alpha'$ -dichlorodimethyl ether; also formaldehyde and quinone.

Such subsequent structural variations which, if they occur less fundamentally or in several stages, may be realised or induced before the shaping operation, but in many cases at the same time as the shaping or subsequently thereto, are, although less pronounced, occasionally possible also in products with only two-dimensional unbranched chains, especially when groups with certain specific reactivity are comprised. Such groups are, for instance (especially end-groups) of the phenolic kind as well as primary carbamide groups, guanidine groups and biguanide groups. Since these reactions are generally limited to end-groups, there is no danger that the elasticity of the structure will be lost by too profound a network. After-treatment with freely reactive substances, for instance, formaldehyde, may with advantage be undertaken in connection with an improvement of the shaped structure, for instance a stretching operation, in which latter case the variation of form must be accompanied by a fixing.

The presence of the polymerization accelerator of saline or salt-forming character or a conversion product thereof does not disturb in general the working-up of the product of the process, and its shaping to the desired structure. Occasionally, indeed, it may be attended by certain advantages, for example when the object is to produce staple fibres which, for facilitating their spinning, ought to be strongly crimped. In other

cases, to be sure, the catalyst residue favours the coloring of the material and at the same time corrosion of the apparatus may occur. A coloring effect is produced by the presence of acid accelerators, for example strong acids and salts of strong acids with organic bases, so that the structures obtained from the polymerides adsorb acid dyestuffs very rapidly and in some cases unequally. This fault may be remedied by a preliminary washing before the dyeing, in which the washing liquid may contain with advantage a mild alkali, for example an alkali acetate, borax, ammonia or ammonium carbonate, for the complete removal of the acid anions.

Even if one sets aside this special point in connection with the dyeing, it is in many cases of advantage to add towards the end of the polymerization, if desired before or during the degasification, an alkaline or acid binding agent. Here there come into question also substances which unite with acids or acid groups to form non-ionogenic compounds, and if desired also can give rise to substitution at amino groups.

In this connection there may be named, for instance, alkaline compounds such as ammonia, alkali acetate, alkali stearate. Preferable, however, are the usual organic bases or organic substances which yield such bases, for example salts of the bases with feeble acids or acids which, in comparison with the base, are volatile; for instance amines, amine salts (amine soaps), amides, for example amides belonging to the group of carbonic acid derivatives. Among the amines are especially the polyamines, especially those of high molecular weight, and of resinous character. Particular materials suitable for this stage of the process are cyclohexylamine, cyclohexylamine-oleate, or -stearate, octamethylenediamine, octadecylamine, octadecylamine-acetate, octadecylpolyethylene-imine, resinous condensation products from alkylene-imines and isocyanates, cyclohexylureas, dicyandiamide, melamine, guanidine salts, cyclic and acyclic isourea ethers and isothioureas ethers.

Favourable results are obtained also if for eliminating or compensating acid properties there is added afterwards a reactive alkylating agent and/or aminating agent which reacts with the acid or basic groups present. There may be used either the ordinary alkylating agents of the ester type or substances which yield these, for instance quaternary salts in presence of a separate acid binding agent, for instance magnesium oxide, or with special advantage a cyclic alkylating agent having a tendency to combine with the reactive groups with ring scission. Of these latter the following may be named:

Ethylene oxide, propylene oxide, butadiene dioxide, epichlorhydrin, phenoxypropene oxide, para-phenylene-dioxypylene oxide, piperidopropene oxide, N-didecyl-methylaminopropene oxide, propylene sulphide, butadienedisulphide, ethyleneimine, N-cyclohexylethyleneimine, N-butylethyleneimine, C-phenyl-ethyleneimine, dodecylethyleneimine. The alkylene-imines and their derivatives react particularly freely if the substratum contains ionogenic halogen.

Insofar as the added reactive substances containing basic nitrogen are fixed in this structure, so that they cannot be washed out or themselves react with the polymeride, there is simultaneously obtained an increase in the total affinity which is desirable for attaining dyeing properties similar to those of vegetable fibres, especially

when the material worked has a high degree of polymerization.

If the first desideratum is to enhance the basic character of the artificial material, polyamines of high molecular weight or high degree of polymerization may be used which can react with the lactam polymerisate without formation of amide, for example those having exclusively tertiary basic nitrogen or even polyamines of high molecular weight in the form of any desired salt so far as these are miscible with the molten mass or the solution, for instance salts of polymeric alkylene polyamines with organic sulphonic acids. It is of especial advantage to use salts when the free amine bases are not sufficiently stable to heat.

The application of the products in form of films, filaments and the like takes place according to known processes: di-casting, casting from the melt or from solutions, drawing from the molten mass or under pressure below the softening point, warm- and cold stretching, rolling in order to effect an orientation of the molecules in one or several directions, etc.

EXAMPLE I

16 grams ϵ -aminocaprolactam are well mixed in a glass tube with 4 grams carefully dried phenylalanine and heated up within an hour at 220° with exclusion of air. After 8 hours heating a feebly colored viscous melt is obtained, which after cooling solidifies into rods of slightly yellow-red color and of great hardness. By careful remelting films may be drawn directly from the melt.

EXAMPLE II

8.1 grams ϵ -aminocaprolactam and 1.9 grams phenylglycocoll are polymerized as in Example I. The slightly brown tinted reaction mass may be transferred from a solution in formic acid (0.5 grams for 1.5 cc. formic acid) into a feebly milky film.

EXAMPLE III

18 grams ϵ -aminocaprolactam and 2 grams tyrosine are heated in a vacuum of 150-200 mm pressure for 7 hours at 220°. The brown reaction mass may be formed into fine filaments in a known manner under slight excess pressure by a spinning nozzle with fine boreholes. If these filaments are simultaneously stretched at room temperature, they assume high tenacity and high tensile strength.

EXAMPLE IV

150 grams ϵ -aminocaprolactam of the diffusion point 69/72° are mixed with 50 grams anthranilic acid, recrystallized three times from methanol, carefully melted together in a glass vessel and placed in an electrically heated oil bath. The air in the reaction vessel is replaced by carbon dioxide freed from air. The reaction product is heated within half an hour at 200°C in an atmosphere of carbon dioxide and kept at that temperature during 5 hours. A high viscous, bright and colorless melt is formed, which may be drawn directly to clear films of high tenacity and good tensile strength. The softening point lies at 205-210°C.

EXAMPLE V

If a mixing proportion of 350 grams ϵ -aminocaprolactam and 60 grams of anthranilic acid is used and the heating carried out under the same conditions, molten masses are obtained, the softening point of which lies about 10° higher. A reaction product of the same qualities is ob-

tained if instead of in a carbon dioxide atmosphere the mass is heated in a vacuum of about 50 mm. If a sealed reaction tube is applied and the water, which is formed during the reaction not eliminated, the resultant high polymeric melt is of a feebly brown tint.

EXAMPLE VI

180 grams ϵ -aminocaprolactam are melted together with 120 grams anthranilic acid under the precautions described in Example IV and heated during 6 hours at 200°C. Instead of supplying the apparatus with a continuous stream of car-

bon dioxide, it is sealed by quicksilver after a complete removal of oxygen, which allows an excess pressure of about 30-50 mm, but blows off at higher temperature. The softening point of the reaction product lies between 195 and 200°C.

EXAMPLE VII

18 grams ϵ -aminocaprolactam are melted together under carbon dioxide with 2 grams p-aminobenzoic acid and heated for 6 hours at 190-200°C. The hard, feebly brownish melt yields clear films of good mechanical strength.

MAX HAGEDORN.



ALIEN PROPERTY CUSTODIAN

PRODUCTION OF VINYL ACETYLENE

Robert Stadler, Heidelberg, and Albert Auerhahn,
Neckargemuend, Germany; vested in the Alien
Property Custodian

No Drawing. Application filed March 16, 1940

The present invention relates to improvements in the production of vinyl acetylene. More particularly, it relates to improvements in the catalysts used to convert acetylene into vinyl acetylene.

For the manufacture and production of vinyl acetylene by the dimerization of acetylene in the liquid phase, it has already been proposed to employ as contact liquids aqueous solutions of cuprous chloride. In operating this process, there are formed besides vinyl acetylene also high molecular tarry and resinous by-products which cause a decrease in the catalytic activity of the cuprous chloride solution. The addition of acids to the cuprous chloride solution in order to increase the serviceable life thereof, may prevent a rapid decrease in the catalytic activity; however, it does not dispense with the necessity of regenerating the catalyst.

We have now found that cuprous chloride contact solutions which have been used in the production of vinyl acetylene from acetylene may be easily regenerated by heating them together with hydrochloric acid. Cuprous chloride solutions treated according to our invention may again be used in the production of vinyl acetylene, if desired, after having converted cupric chloride which may be present into cuprous chloride. This surprising result involves the great advantage that the difficulties and inconveniences connected with the known regeneration of spent cuprous chloride solutions by means of chlorine can be dispensed with altogether.

In carrying out our invention, we add concentrated hydrochloric acid to the spent cuprous chloride solution. The amount of concentrated hydrochloric acid may vary considerably. We prefer to add an amount corresponding to from about 1 to 15 per cent of the weight of the spent solution. Instead of adding concentrated hydrochloric acid, we may introduce a corresponding amount of gaseous hydrogen chloride thereby forming hydrochloric acid within the contact solution.

The mixture of spent contact solution and hydrochloric acid may then be allowed to stand for some time. It is then heated, preferably below its boiling point, generally speaking within the range of from about 60 to 95° C. The heating may be discontinued, when a sample withdrawn from the solution yields, after filtration and addition of water, a pure cuprous chloride precipitate. During the heating, the presence of oxygen should be excluded in order to prevent the oxidation of the cuprous chloride. It is also preferable to ex-

clude free acetylene which may form undesirable by-products.

The solution contains a certain amount of a voluminous precipitate wherein a small amount of copper or copper compounds are embodied. Before using the solution again for the production of vinyl acetylene, this precipitate is separated off, preferably by filtration. The copper contained in the precipitate may easily be converted into cement-copper.

The filtrate may be used without further treatment immediately for the conversion of acetylene into vinyl acetylene. If the filtrate contains substantial amounts of cupric chloride, powdered copper may be added in order to reduce this to cuprous chloride.

The regeneration of contact solutions may be carried out continuously even without interrupting the production of vinyl acetylene. This may be done, for example, by branching off part of the contact liquid, adding thereto hydrochloric acid, heating it, preferably in the absence of substantial amounts of oxygen and acetylene, separating off the precipitate, adding, if desired, fresh cuprous chloride corresponding to the amount of copper contained in the precipitate, and leading back the solution into the reaction vessel.

Our invention will be illustrated in the following examples in respect to cuprous chloride solutions containing ammonium chloride. It will, however, be understood that our novel process is likewise applicable to other contact solutions capable of promoting the conversion of acetylene into vinyl acetylene and containing besides cuprous chloride another ammonium salt or an amine salt or also an acid constituent.

Example 1

Into a solution consisting of 147 kilograms of cuprous chloride, 90 kilograms of ammonium chloride and 150 liters of water there are led per hour 32 cubic meters of acetylene. The yield of vinyl acetylene amounts to 34 grams per hour for 1 kilogram of cuprous chloride; the concentration of vinyl acetylene in the reaction gases is 71 per cent. This rate of conversion steadily decreases. After it has reached 25 per cent and after the contact solution starts to foam, the process is discontinued. The solution is allowed to stand for three days at room temperature, while excluding air. For 1 liter of the solution 30 cubic centimeters of commercial hydrochloric acid (36 per cent) are added and the whole is heated to 80° C for 5 hours. The solution is filtered off and

1 kilogram of powdered copper and 1.5 kilograms of solid cuprous chloride are added to the greenish-black colored filtrate. It is then again used as contact liquid. When leading acetylene into the solution under the conditions referred to above, 42 grams of vinyl acetylene per hour for 1 kilogram of cuprous chloride are obtained. The concentration of vinyl acetylene in the reaction gases now amounts to 80 per cent.

Example 2

A column is charged with a mixture of 110 kilograms of cuprous chloride, 75 kilograms of ammonium chloride, 1 kilogram of powdered copper and 110 liters of water. 30 cubic meters of acetylene per hour are led through the contact liquid at 90° C. When the decrease in the yield of vinyl acetylene indicates that the reaction has

slowed up, 10 per cent of the contact liquid are withdrawn into a separate vessel which is heated to from 70 to 80° C. 10 cubic centimeters of 36 per cent hydrochloric acid are added for 1 liter of the cuprous chloride solution and a current of nitrogen is led through the solution. After about 15 minutes a sample withdrawn and filtered yields a pure cuprous chloride precipitate when diluted with water. The bulk of the solution is then filtered and given back into the column.

This regeneration is repeated as soon as the activity of the contact liquid decreases substantially. From time to time, the total loss of cuprous chloride is determined and a corresponding amount thereof added to the contact liquid.

ROBERT STADLER.
ALBERT AUERHAHN.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR CONCENTRATING AQUEOUS DISPERSIONS

Arend d'Angremond and Otto Bertram Schrieke,
Medan, Sumatra, The Netherlands East Indies;
vested in the Alien Property Custodian

No Drawing. Application filed March 27, 1940

The invention relates to the concentrating of very different kinds of aqueous dispersions. In industry this concentrating is of special importance for thickening rubber latex, but also for thickening milk and the preparation of cream.

It is already known that such dispersions can be concentrated by evaporating, filtrating, centrifuging, by applying so-called creaming agents, or by freezing. However, these known methods present several disadvantages. The majority of these treatments require expensive apparatus. Moreover in most cases, one obtains a concentrated dispersion which no longer shows the same qualitative composition as the original liquid. For by centrifuging and creaming, the dispersion loses certain of its components, while in methods such as evaporation, filtration, or the application of creaming agents, it is first necessary to add to the dispersion alien substances such as protective colloids, anticoagulants, antioxidants, creaming agents, which are to be found again in the concentrate. Finally freezing a dispersion presents great difficulties, especially in the tropics.

According to the present invention, a concentrate is quickly obtained, which not only still contains all the non-aqueous components originally present in the unconcentrated liquid, but to which no new substances, or only a small quantity of them, are added.

The invention is based on the principle that the desired increase in concentration of the dispersion can be obtained by bringing the liquid into contact with those parts of plants, which have a high capacity of absorbing water, such as seeds, dried fruits, tubers, bulbs, roots, leaves, parts of stems etc. The best results in this connection are obtained with seeds, because the other parts of plants mentioned some times have the disadvantage of bruising or even being pulverised during the treatment, whereby sieving the drying material is rendered difficult and the dispersion is soiled. The use of seeds is further advantageous because the skin of seeds is easily permeated by water, whereas many other substances do not permeate it. Consequently, on the one hand, no components are withdrawn from the dispersion, while on the other hand, matter from the seeds is prevented from entering the dispersion.

Many seeds, when placed in an aqueous dispersion, were found capable of extracting a large amount of water from this liquid. The quantity of water which can be absorbed by the seed, varies with the sort used; in several cases it amounts to 100-150% of the weight of the air-dry seeds.

Therefore only seed will be used as example in the further specification.

The process according to the invention is preferably carried out as follows: The dispersion to be concentrated is put into a closed cylindrical vessel, which can rotate round its horizontally placed axis. The desired quantity of seed is weighed and likewise put into the vessel; then this is closed and put into motion.

The seeds now begin to swell, that is to say they extract water from the liquid, whereby on the one hand they grow in volume, and on the other hand the dry substance percentage of the dispersion increases. The rotation ensures that the seeds are continually brought into contact with another part of the liquid; moreover, the solid substances of the dispersion are thereby prevented from depositing themselves in a layer of poor permeability on the seed skins, which would retard the absorption of water. After a number of hours, e.g. eight, the seeds have extracted the maximum quantity of water from the dispersion. The rotation is then stopped and one drains off the thickened dispersion.

One is often restricted in the choice of the seed to be used, because many seed skins contain colouring-matter soluble in water, which would as a rule discolour the dispersion undesirably. This difficulty can be met with by using colourless seeds, or seeds without colouring-matter soluble in water. And again, some seeds have a very hard skin which impedes the absorption of water. In this case the seeds can be subjected beforehand to one of the well known methods such as mordanting, scouring off or slitting, through which the skin, all over, or in certain places, becomes more permeable.

The invention is made considerably more economical in its application, because after finishing the concentrating, the parts of plants, for instance the seeds are rinsed and then dried. After this they can be used again for a further treatment. As this drying and then swelling again, if done carefully, can be repeated several times without unfavourably affecting the capacity to absorb water, the consumption of the water extracting substances, for instance seed, is thus very much reduced.

The drying of the seed can be done by several methods. The simplest way is to spread the seed over a large surface and to let it dry in the sun. In case one wants the drying done in a quicker way, one can successfully use one of the methods in which a current of heated air is passed along

the substance to be dried for instance on special drying-lofts, drying-frames, in fruit-driers etc.

In many cases it will be desirable to add a preservative to the dispersion before the thickening according to the invention begins. The known agents, which are also used in the other methods of concentration can be applied therefor. In the case of rubber latex, ammonia is preferably used; at the same time this agent prevents the latex from coagulating during the treatment. By adding ammonia to the dispersion one also ensures that the seed does not germinate during the treatment. In case one wants to prevent this germinating when ammonia is not used, this can be done by killing the seed beforehand, e. g. by treating the seed with hot water or with an aqueous solution of formaldehyd or of chlorine during some hours. It has been observed that killing the seed beforehand has no unfavourable influence on its capacity to absorb water.

The properties of concentrates prepared according to the invention greatly resemble those of the products obtained by evaporation of the water. For then also, all the components of the original dispersion are still present in the concentrate. However, the addition of protective colloids,—as is usually necessary in the evaporation process, and whereby the properties of the dispersion are also influenced,—can be omitted in the process according to the invention.

If required the process according to the invention can be combined with one of the known methods for the concentrating of dispersions.

The process will be further illustrated by the following examples.

Example 1

1800 cm³ of plantation latex, to which as preservative so much ammonia was added, that the NH₃ content calculated on the latex was 0.75%, and which had a dry rubber content of 37.86%, was equally distributed in 18 bottles which could be closed. Thereupon different quantities of soja beans (*Glycine Max* Merr.) were put into these bottles. The bottles were now placed in an apparatus, which kept their contents in continuous motion. After respectively 4 hours, 8 hours and 24 hours, the experiment was interrupted and the contents of 6 bottles at a time were analysed according to the following scheme. The result of these tests was as follows:

Number of grams of seed added to 100 cm ³ latex	Dry rubber content of the concentrate in percent.		
	After 4 hrs.	After 8 hrs.	After 24 hrs.
5	39.84	40.44	40.60
10	41.78	43.18	43.06
20	45.30	49.46	49.38
30	49.10	54.76	54.46
40	52.82	60.86	
50	54.34	61.60	

From the above it is apparent, that the con-

centration of the dispersion can be increased at will by regulating the amount of seed to be added. If one takes larger quantities of seed than the maximum mentioned in the table, one soon gets a paste which can only be separated from the seed with difficulty.

The table also shows, that after eight hours of rotation practically no further increase of concentration is obtained.

Example 2

Latex with a dry rubber content of 34.65% was creamed with the aid of an aqueous dispersion of the flour of *Amorphophallus-tubers* (see for instance *The Netherlands Patent No. 37 288*). The cream obtained in this way was drained off after four days. The dry rubber content of the cream appeared to be 52.06%.

To 150 cm³ of this cream sufficient ammonia was added to make its content 0.7%; thereupon the mixture was placed in a bottle, in which 30 grams of peas (*Pisum Sativum* L.) had already been weighed. The bottle was then closed and slowly rotated. After 4½ hours the bottle was opened and the very viscous concentrate of the seed was separated and analysed. The dry rubber content now appeared to have increased to 67.80%.

Example 3

12 kg latex, to which 0.7% ammonia had been added as preservative, were put into a cylindrical closed vessel. 2.5 kg soja beans were then added. Hereupon the vessel was closed and rotated. The test was terminated after 8 hours. The original latex had a dry rubber content of 31.06%; 8.8 kg of concentrate with a dry rubber content of 41.58% were obtained.

Example 4

To 5 bottles, each containing 100 cm³ conserved cow's milk, were respectively added:

	Grams
(1) Soja beans	20
(2) Soja beans	30
(3) Soja beans	40
(4) Seeds of <i>Vigna sinensis</i> Endl.	30
(5) Green peas	30

After 8 hours of rotation the dry substance content of these samples was determined. The result was:

Sample	Dry substance in percent
Non-treated milk	13.62
(1)	17.85
(2)	21.07
(3)	25.05
(4)	19.12
(5)	81.60

This table shows that cow's milk can also be excellently thickened according to this process.

AREND D'ANGREMOND.

OTTO BERTRAM SCHRIEKE.

ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING STARCH ESTERS

Martinus Gerardus Groen, Hoogezand, The Netherlands; vested in the Alien Property Custodian

No Drawing. Application filed March 28, 1940

Several methods for the production of fatty acid esters, more particularly acetic acid esters, from starch have been proposed. These esters have properties which are similar to those of the cellulose esters and therefore may be used to a certain extent for the same purposes. Up to the present, however, it has not been possible to obtain a satisfactory yield of starch esters having a sufficient degree of esterification, i. e. that contain at least $2\frac{1}{2}$ acyl groups per molecule of $C_6H_{10}O_5$.

In general starch in gelatinized condition is very hard to esterify with acids or acid anhydrides, while moreover by the high temperature required for this esterification there are formed products which, on account of the decomposition of the starch molecules, have become partly water soluble and therefore are inferior from a technical point of view. The production of formic acid esters is more easy; these esters, however, are unstable and are technically of minor importance. It is also possible to produce starch esters by means of acid chlorides in the presence of organic bases.

It is known that esterification will proceed more readily, if the starch has been previously gelatinized or brought into a soluble form. It has been proposed i. a. to subject the starch before the conversion into fatty acid esters to a swelling treatment with chloroacetic acid or alternatively to bring the starch into a soluble form by the action of glycerol at 160°C . The action of the catalysts generally used in acetylating processes, such as hydrohalogenic acids, sulfuric acid, aluminium chloride, zinc chloride and the like, is also to be considered as being chiefly due to their property of rendering the starch soluble. These catalysts are not very suitable for the preparation of technically valuable starch esters, as they generally are apt to decompose the starch too far, and the yield is generally too low.

The formic acid esters mentioned above are easily produced, since starch is soluble in concentrated formic acid. If this solution is treated with acetic acid and acetic acid anhydride, there will be formed an ester which contains a formyl group and an acetyl group in each molecule of $C_6H_{10}O_5$, but which will not dissolve in organic solvents, so that these products also are as yet of little value in actual practice.

According to the invention it is possible to prepare technically valuable esters from starch with fatty acids and/or hydroxy fatty acids by treating the starch which has been dissolved in an anhydrous medium in the presence of an acetate

with the acids in question, or with the anhydrides thereof.

A solution suitable for this purpose may be obtained in the manner described above with the aid of formic acid. It has been found that when treating such a solution with e. g. acetic acid anhydride or with a mixture of acetic acid and acetic acid anhydride in the presence of sodium acetate a substantial decomposition of the starch will not occur, even at high temperatures, and that products are obtained thereby that are esterified to a very high degree and are containing e. g. 2.8 acetyl groups.

It is, however, also possible to start from other starch solutions in an anhydrous medium. According to an embodiment of the invention the starch is dissolved in a mixture of ammonium acetate and acetamide and subsequently acylated with acid anhydrides or mixtures of acids and acid anhydrides. The mixture of ammonium acetate and acetamide may be obtained by saturating acetic acid anhydride with ammonia gas, and it has been found that starch may be readily dissolved in this mixture at a temperature of e. g. 140°C . By the acylation of the dissolved starch the esters are produced in a substantially theoretical yield; the composition of the esters depends i. a. on the proportion of the acylating agent, the temperature and the time of reaction.

The reaction may be promoted by distilling off, preferably in vacuo, the water formed, by the reaction either during the treatment or during the first phase of the said treatment.

By the acylation described above a yield of 95% of esters containing up to 2.8 acyl groups, e. g. acetyl groups, is obtained. Efforts to obtain the pure triacetates by using a larger proportion of acetic acid anhydride have failed because of an initial saponification. It has been found, however, that by adding per-compounds, especially hydrogen peroxide, at the end of the reaction it is possible to produce the tri-ester without any difficulty, which most likely is due to the formation of per-acetic acid. Moreover, the hydrogen peroxide has a bleaching action, so that very light colored esters are obtained.

The use of sodium acetate as a catalyst in acetylating processes is not novel per se; this catalyst, however, has not yet been used for producing starch esters containing more than 2.5 acyl groups.

Example

100 parts by weight of acetic acid anhydride are saturated with dry ammonia gas. In the

reaction mixture 30 parts by weight of anhydrous sodium acetate and 32 parts by weight of dried potato starch are dissolved. The mixture is heated to 140° C for one and a half hours, and 50 parts by weight of acetic acid anhydride are slowly added while agitating. After the agitating treatment has been continued for an hour, the water is distilled off in vacuo, after which the addition of acetic acid anhydride is continued until 100 parts by weight have been added in total. When pouring the reaction mixture into water an ester containing from 2.5 to 2.75 acetyl groups is obtained.

The treatment is preferably continued, however, by further agitating the reaction mixture without heating, prior to pouring the same into water and by adding 35 parts by weight of a 5% solution of hydrogen peroxide and 5 parts by weight of acetic acid anhydride. The reaction mixture which will be very light in color is left over night and then poured into water, whereby the tri-ester is precipitated. The precipitate is

washed and dried subsequently. This ester is perfectly soluble in organic solvents and the solutions are homogeneously miscible with solutions of acetyl cellulose.

Besides fatty acids such as acetic acid one may also use hydroxy fatty acids, e. g. lactic acid, for the esterification. It is possible in this manner to prepare mixed esters, in which the hydroxy groups of the starch are esterified e. g. partly with lactic acid and partly with acetic acid.

The method according to the invention is chiefly important for the production of highly esterified products from non-converted starch, particularly potato starch. It is also possible, if desired, to start from starch products which have been subjected to a treatment whereby esters are produced the properties of which are more or less different from those of the esters of the original starch. Very suitable products may be prepared e. g. from cold swelling starches.

MARTINUS GERARDUS GROEN.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR MANUFACTURING CARBINOLS HAVING AN ACETYLENIC FUNCTION

Joseph Zeltner and Michailas Genas, Paris, France; vested in the Alien Property Custodian

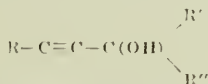
No Drawing. Application filed March 29, 1940

It is known that carbinols with an acetylene function can be obtained by the action of substances possessing a carbonyl group $\text{C}=\text{O}$, either on the acetylides of alkali metals, or on organo-metallic derivatives of acetylene or substitution products of the latter.

The first method offers serious drawbacks for carrying it out industrially, since it requires very low temperatures, of the order of -30° to -40°C. , solvents such as liquid ammonia, and the use of expensive products such as metallic sodium or sodium amide.

The second method, that is to say the preparation by means of organo-metallic substances, is practically inapplicable industrially.

It has also been proposed to obtain acetylene carbinols, such as phenylacetylene derivatives, by reacting the latter with acetone in the presence of powdered potash, the products resulting from this reaction being carbinols of the general formula:



It has also been proposed to replace the substitution products of acetylene by acetylene itself. This reaction was effected in the presence of ethyl ether as a solvent. But this solvent has serious drawbacks from the industrial standpoint, owing to its volatility, its inflammability and the dangers of explosion that may be caused by the formation of peroxides. This danger may be increased, in the applications in question, since said peroxides may react with the acetylene compounds formed and produce substances which are particularly explosive.

We have found, and this is what the invention consists in, that the reaction of acetylene or mono-substituted acetylene with products containing a carbonyl group, in the presence of solid potash, for forming acetylene carbinols, can be effected in certain solvents, other than ethyl ether, which do not have the serious drawbacks of the latter.

The solvents which enable the reaction in question to be effected must contain atoms such as trivalent nitrogen, bivalent oxygen, or other atoms capable of changing to a higher valency. Such solvents may, for example, be ether-oxides, acetals, tertiary amines, etc.

In order that the reaction shall take place under satisfactory conditions and with maximum efficiency, it is preferable to mix the potash beforehand with the above mentioned active sol-

vents, at a suitable temperature which depends on the nature of the solvent. I have found that this method of proceeding favours the subsequent formation of the potassium derivative.

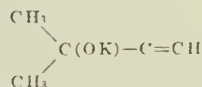
It is advisable to form a certain quantity of this potassium derivative by introducing a part of the acetylene substance before beginning to introduce the substance containing a carbonyl group it is desired to combine therewith.

We then continue to introduce the substance having an acetylene function, so as to keep the whole or a part of the initially formed quantity of potassium derivative in the reaction mixture.

Example 1

175 parts of powdered potash are mixed with 250 parts of dimethylformal, performing the function of an active solvent, at a temperature of about 15°C. , and the temperature is allowed to rise to about $30-35^\circ \text{C.}$ The mixture is cooled to about 0°C. , then about 10 parts of acetylene are introduced. Then 60 parts of acetone are gradually added and 23 further parts of acetylene.

The potassium derivative of the corresponding acetylene carbinol is formed:



Decomposition is effected with water and, after the evolution of the excess of acetylene and the separation of the aqueous layer, the solvent is separated from the carbinol formed, by distillation.

About 80 parts of carbinol are obtained, whereof the boiling point is $104-106^\circ \text{C.}$

Example 2

450 parts of diethylaniline are mixed with 175 parts of powdered potash. After introducing 4 parts of acetylene into this mixture, 60 parts of acetone are added, and the introduction of the acetylene is simultaneously continued. After adding 16 parts of acetylene, the reaction product is decomposed with water and the operation is continued as in the previous example.

Example 3

175 parts of powdered potash are mixed with 500 parts of dimethylformal, at a temperature of about 15°C. and the temperature is allowed to rise to about $30-35^\circ \text{C.}$ The mixture is cooled to about 0°C. , then about 20 parts of acetylene are introduced. 45 parts of acetaldehyde in solution in 100 parts of dimethylformal are then grad-

ually added, and the introduction of acetylene is simultaneously continued. After adding 10 parts of acetylene, the reaction product is decomposed with water, and the operation is continued as in example 1.

Methyl-acetyleneyl-carbinol having the formula:



is thus obtained, whereof the boiling point is 103– 105° C.

Of course, the examples given are purely explanatory and in no way limitative, and it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is therefore aimed in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

JOSEPH ZELTNER.
MICHAELAS GENAS.

ALIEN PROPERTY CUSTODIAN

HIGH-MOLECULAR FILM-FORMING CONDENSATION PRODUCTS AND PROCESS OF PRODUCING SAME

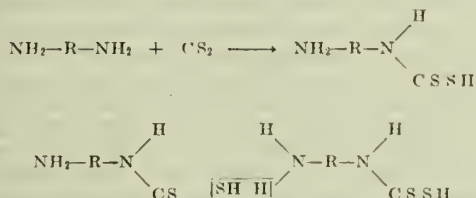
Rudolf Kern, Ludwigshafen-on-Rhine, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed March 30, 1940

The present invention relates to high-molecular weight film-forming condensation products and a process of producing same.

I have found that high-molecular film-forming condensation products are obtained by reacting carbon disulphide with aliphatic diamines, the amino groups of which are separated from each other by at least 5 carbon atoms and heating the dithiocarbamic acids formed at temperatures of between 60 and 300° C, preferably from 120 to 200° C, whereby hydrogen sulphide is split off.

The reaction is likely to take the following course:



The latter formula shows the first step in the further condensation of the dithiocarbamic acids which proceeds with the splitting off of hydrogen sulphide and the formation of the dimer; this dimer, by reacting with another molecule of dithiocarbamic acid or the dimer thereof, forms higher molecular products until by continued heating film-forming condensation products are formed.

As initial material such aliphatic diamines are used as bear their amino groups separated from each other by more than 4 carbon atoms, as for example pentamethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, undecamethylene diamine and dodecamethylene diamine. Diamines, the carbon chain of which is interrupted by hetero atoms such as oxygen or sulphur or atomic groups as for example the NH-group may also be used. The corresponding alkyl-, aryl- or aralkyl-substituted diamines which still contain at least one hydrogen atom attached to each nitrogen atom may equally be employed. Alternatively, alkyl, aryl or aralkyl groups may also be introduced into the dithiocarbamic acids first obtained before they are further condensed.

Besides or instead of carbon disulphide there may also be employed thiophosgene, in which case dithiocarbamic acid chlorides are formed in the first stage of the reaction, hydrogen chloride being evolved; carbon disulphide, however, is preferred on account of its greater ease in manipulation.

The dithiocarbamic acids are prepared by causing carbon disulphide to act upon the diamine at ordinary temperature. It is advantageous to use a diluent, such as water, methanol or ethanol.

The dithiocarbamic acids are generally obtained in the form of colorless crystals.

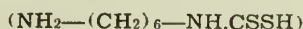
The further condensation of the dithiocarbamic acids which proceeds with the splitting off of hydrogen sulphide may be carried out depending on the final products obtained under atmospheric, reduced or superatmospheric pressure either in the presence or absence of solvents or diluents. Instead of heating the acids themselves their salts, preferably their alkali salts may be heated for further condensing. Thus, for example, when heating a solution of the dithiocarbamic acids in soda lye, the same products are formed. Air is preferably excluded, because it sometimes causes side-reactions and discoloration of the reaction products.

The reaction products are fusible and may be drawn into threads when working under mild conditions, and are infusible when working under more energetic conditions. The high-molecular weight condensation products obtained may be used for a great variety of purposes, either alone or in combination with other suitable substances, for example for the production of films and threads, coatings, adhesives, putties and in the manufacture of safety glass, furthermore as assistants in the textile, artificial leather and paper industry as well as for the manufacture of pressure-moulded or injection-moulded articles.

The following Examples serve to illustrate the nature and the properties of the products in accordance with the present invention and the methods of their production. The invention, however, is not restricted to these Examples. The parts are by weight.

Example 1

116 parts of 1,6-hexamethylene diamine are dissolved in 1000 parts of ethanol of 96 per cent strength and 145 parts of carbon disulphide are slowly introduced at 0° C. To prevent formation of supersaturated solutions and consequent separation of the reaction product in an oily state, it is preferable to add crystals of dithiocarbamic acid formed in a preceding batch. The dithiocarbamic acid formed thus separates as beautiful colorless crystals. They are filtered off by suction and washed with alcohol or water. For further purification, which, however is not necessary, they may be recrystallized from ethanol or water. The pure dithiocarbamic acid



melts at between 156° and 158° C.

When causing the aqueous solution of the dithiocarbamic acid to boil for some time, hydrogen sulphide is split off and an oily product which is insoluble in water, separates. It is soft and plastic at ordinary temperature. It is readily soluble in formic acid. It cannot be precipitated

quantitatively by water, but forms a gel by the addition of water.

By heating the substance separated by boiling the aqueous solution of the dithiocarbamic acid or heating the pure dithiocarbamic acid itself in the form of the colorless crystals (melting point 156 to 153°) above 160° C for a longer space of time, there takes place a further or first splitting off—as the case may be—of hydrogen sulphide, tough melts being thus formed. This melt may be drawn into threads which on stretching in the cold state may be orientated whereby their tensile strength is considerably improved. Furthermore the melt may be cast or drawn into ribbons or films, which may be orientated by rolling and thus improved. The product is still soluble in formic acid and may be precipitated with water. After drying it is a hard, crumbly, tough and elastic material.

By further heating the melt the condensation may be carried on until practically infusible pale products are obtained which in the cold state are very hard and hornlike masses. They may be used for the manufacture of a great variety of articles, either by working them with cutting tools or by pressing them hot. In this state the product is no more or but little soluble in formic acid.

The condensation of the dithiocarbamic acid which proceeds with the splitting off of hydrogen sulphide may also be carried out in the presence of solvents or diluents. The high-molecular condensation product formed thereby sometimes separates similarly as when condensing in water. Suitable solvents or diluents are, for example, pyridine, quinoline, hexahydrodiethylaniline, xylene, tetrahydronaphthalene, glycol or glycerine.

Example 2

28.6 parts of octamethylene diamine are dissolved in 250 parts of ethanol and cooled down

to 0° C. A mixture of 17 parts of carbon disulphide and 50 parts of ethanol is then dropped in very slowly, while stirring, to prevent formation of undercooled solutions, the temperature being maintained between 0 and 10° C. After a short time the 1-amino-octamethylene-8-dithiocarbamic acid begins to precipitate in the form of very fine and colorless crystals. The solution is further stirred for some hours while cold, the crystals are then filtered off by suction, again suspended in ice-cooled ethanol, filtered and dried. The pure acid melts at between 145 and 147° C with decomposition. On heating the acid to 160° C in the absence of air hydrogen sulphide is split off, a high-molecular condensation product being formed which is suitable for use as a plastic.

Example 3

81.6 parts of butane-diol-1.4-di-normal-propyl-ether- ω,ω' -diamine (corresponding to the formula

$$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OCH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$$

are dissolved in 400 parts of ethanol, whereupon a mixture of 31 parts of carbon disulphide and 100 parts of ethanol is slowly run in, the temperature being maintained between 0 and 10° C. The dithiocarbamic acid precipitated is filtered off by suction after about 12 hours, twice washed with ice-cooled ethanol and dried. The yield amounts to 92 per cent of the theory; the acid melts at 104° C with decomposition. The acid is dissolved in a 25 per cent caustic soda solution and the clear solution which results is heated to boiling. After some time the insoluble condensation product begins to separate on the lye. It is removed, washed with boiling water until neutral and dried. It may be used as a plastic for the preparation of coatings or moulded articles or as an addition for coatings and plastics.

RUDOLF KERN.

ALIEN PROPERTY CUSTODIAN

METHODS OF REGENERATING VULCANIZED RUBBER

Umberto Sartorelli, Milano, Italy; vested in the Alien Property Custodian

No Drawing. Application filed March 30, 1940

This invention relates to the art of reclaiming rubber, and more particularly refers to improvements in methods of regenerating vulcanized rubber scraps.

It is well known that vulcanized rubber scraps may be plasticized and made available for reprocessing by the ordinary methods of rubber goods manufacture. The process of treatment is known as reclaiming, and the product as reclaimed rubber, reclaim or shoddy.

Many method have been devised. However, all the processes heretofore used on a commercial scale were based essentially upon the depolymerizing action of heat on the rubber itself. Processes in which heat as a depolymerizing agent is used in the presence of substances assisting the regeneration of the rubber are extensively applied. Among these, the most widely known and applied is the alkali process, which consists in heating ground scrap with a dilute solution of caustic soda at temperatures about 350° F. for twelve to twenty hours, and similar processes, in which sodium sulphite and bisulphite, or else magnesium sulphate, zinc chloride, etc., are used instead of the sodium hydrate.

Processes in which small percentages of plasticizing substances of various characters are added to the vulcanized scrap are also known; however, these substances are not eliminated during regeneration, and while they impart to the product some particular characteristics these are always obtained at the expense of its mechanical properties.

Solution processes in which the vulcanized scrap is dissolved by the aid of solvents while subjected to high temperatures, for instance, 175° C., but at any rate never less than 120° C., have also been suggested, the solvent being subsequently recovered by suitable treatment, leaving as a result the reclaimed or regenerated product. These processes have also had some practical application but have not received wide acceptance, because the regenerated products resulting thereby have poor mechanical characteristics. In addition, there are processes representing modifications of such solution processes, in that the dissolving operation is interrupted at a somewhat earlier stage, as soon as the product is capable of being dispersed in water, the treating agents being also in these cases recovered, and the rubber being coagulated from the aqueous emulsion by suitable means.

The primary object of this invention is to provide a novel and improved method of treating vulcanized rubber scrap, whereby a regenerated

product of superior quality, practically comparable to crude rubber, is obtained.

Another object is to provide a method of regenerating vulcanized rubber scrap, entailing a succession of relatively simple steps, making it possible not only to produce a superior product, but also to recover the various agents used in the treatment, practically in their entirety.

A further object is to provide a novel and improved method of regenerating vulcanized rubber scrap, whereby the reclaimed product is practically free of the plasticizing agents which might have been present in the original mixture, as well as of the resinous substances resulting from the natural aging of the vulcanized material, or due to the harmful effects of a possible oxidation during the drying operation.

A still further object is to provide a method of treating vulcanized rubber scrap, whereby it is possible to obtain a reclaimed product having a very low acetic content, in which the original characteristics of the rubber have been restored virtually in their entirety.

Other objects and advantages of the present invention will more fully appear as the description proceeds and will be set forth and claimed in the appended claims.

The method forming the subject of the present invention represents a radical departure from all the other processes heretofore known, in that it utilizes the capacity of the vulcanized scrap to expand or swell by absorption of swelling or solvent substances, without being brought even to the initial stages of actual solution.

In the first stage, the material is treated with a swelling or solvent substance, at a low temperature enabling the material to become impregnated with the said substance, without, however, becoming dissolved therein.

In a succeeding stage, in which the regeneration proper of the rubber takes place under the action of heat, the solvent substance is recovered practically in its entirety, its separation from the regenerated product being effected through suitable washings carried out with a liquid capable of dissolving the swelling or solvent substance only, to the exclusion of the rubber. Thus a regenerated product is obtained, having an exceedingly low acetic content, which has been freed not only of the swelling or solvent substance, but also of the plasticizing agents which may have been present in the original mixture, and the resinous products derived from the natural aging of the vulcanized material.

The basic characteristics of this new method

of treatment, therefore, resides in the impregnation, at a low temperature, of the previously ground vulcanized rubber, with a high percentage of a swelling or solvent substance. In this connection, it is well to state that by low temperature, a temperature of less than 50° C. is meant, or in any event a temperature materially lower than that required for bringing the vulcanized rubber into solution. It is to be understood that the term "vulcanized rubber" as used herein connotes any vulcanized rubber composition containing natural or artificial rubber in a vulcanized condition with or without softeners, fillers or any other of the compounding ingredients usual in the rubber industry.

The percentage of swelling or solvent substance which may be employed in this treatment of vulcanized rubber is subject to considerable variations, according to the type of scrap treated and the character of the substance itself. At any rate, its proportion is always very high, usually about 100% of the weight of scrap treated, although in special cases it may assume different values. In practice this proportion is determined by the maximum quantity that the scrap is capable of absorbing, without losing its original form as resulting from the grinding operation.

The swollen scrap is then cooked in an autoclave in the presence of water or of one of the usual devulcanizing agents, such as for instance caustic alkalis, alkaline sulphides, alkaline sulphites and hyposulphites, etc. The pressure and temperature of the autoclave, the duration of the heating period, and the concentration of the alkaline liquid if used, depend upon the character of the scrap to be regenerated.

If the operation has been conducted in the presence of an alkaline agent, upon the completion of the heat treatment in the autoclave, the scrap is washed, and then, after drying, is subjected to the washing operation for the recovery of the swelling or solvent substance employed in the previous stage.

This washing operation, by means of which the swelling or solvent agent is recovered practically in its entirety for re-use in subsequent treatments, acts at the same time as a means of purifying the regenerated rubber, in that, as previously stated, it also eliminates from it the plasticizing agents present in the original mixture and those resinous products which may have been formed as a result of the natural aging of the vulcanized rubber.

The washing ended, the liquid used therefor is also recovered, either by direct heating, or by the action of steam, or in vacuum, according to its particular nature.

The regenerated product is ready eventually to be rendered uniform, and, if necessary, to be refined in any one of the ways known to persons skilled in the art.

The selection of the swelling or solvent agent depends upon the character of the scrap to be treated, and is of primary importance; in any event the liquid used should preferably be capable of ready absorption by the vulcanized material, while being scarcely capable of reacting with water or with the alkaline liquid. Among the solvents best adapted for the purpose may be mentioned the medium heavy and heavy mineral oils, the various high boiling fractions resulting from petroleum distillation, and like substances, vegetable tars and oils deriving therefrom, coal tar and oil derivatives thereof, resin oil, and syn-

thetic liquids obtained through hydrogenation of naphthalene.

It is obvious, therefore, that the liquid required for the washing of the regenerated product and the recovery of the swelling or solvent agent therefrom should be properly selected with respect to the nature of the latter. The liquids used, according to cases, have been aliphatic alcohols, alky-esters, preferably acetates such as amyl acetate, ethyl acetate, butyl acetate, etc., ketones, particularly acetone, or else suitable mixtures of such solvents. In all cases the liquid used for washing should be a solvent of the swelling material, never of the regenerated rubber. Here also it may be stated that although in specific cases it may be preferable to use one liquid rather than another among those of the character mentioned, their action on the solvent agents used in the preceding stage is sufficiently similar to warrant their being considered virtual equivalents for the purposes of the present invention.

By proper selection of the various steps among those used in common practice, it is possible to recover the swelling or solvent agent and the washing liquid in full, and to have a very high rate of recovery of the alkaline liquid, if it has been used.

If the vulcanized rubber scrap to be treated contains fibrous material, the recovery of the alkaline liquid will be somewhat less; but if the fibrous material is removed before regeneration is carried out this undesirable loss will be avoided.

The above mentioned individual steps, if carried out according to the dictates of good practice, will result in the production of regenerated rubber of very high quality, in which the original characteristics have been almost completely restored. Its acetic extract varies between 2 and 3%, never reaching over 5%, the chloroformic extract reaches maximums of high value, and the mechanical characteristics of the original mixture are almost entirely regained.

It is also interesting to observe, that by virtue of the operation leading to the recovery of the swelling or solvent agent, the resinous products due either to the natural aging of the original vulcanized material or to the harmful effects of a possible oxidation during the drying operation, are also automatically eliminated. That this is so is confirmed by the low value of the acetic content, which also gives assurance that the products manufactured with such regenerated rubber will not subsequently age at an unduly fast rate. Furthermore, the regenerated rubber resulting from the new method described is easily workable and easily extruded.

In order to better illustrate my invention, I will now give a practical example relating to the regeneration of 100 kilograms of peelings obtained from old pneumatic tire shoes such as found on the market.

These peelings, in strip form, are ground to pieces of a size somewhat larger than a pea, and these are then placed in a rotating metallic drum together with 100 kilograms of naphtha (petroleum fraction distilling at a temperature over 250° C.). The scrap is left in the drum, at room temperature for about twelve hours, and becomes completely impregnated with the swelling agent without, however, entering into solution.

The scrap thus impregnated is placed in an autoclave in which a 5° Beaumé solution of hydrate of sodium is added in a quantity sufficient to completely cover the scrap. The pressure

in the autoclave is brought to from 12 to 15 atmospheres, and is maintained for about 3 to 4 hours.

When the resulting regenerated product is discharged, the sodium hydrate is recovered by washing with water, and the regenerated rubber is then dried. Once dry, it is placed in an extractor in which, by means of a mixture of amyl-ethyl-butyl acetates, it is freed from the naphtha. The extraction being completed, the naphtha and the mixture of acetates are separately recovered by known methods.

As a final result we have:

	Per cent
Recovery of the sodium hydrate-----	about 90
Recovery of the naphtha-----	about 95
Recovery of the mixture of acetates---	about 98

The regenerated rubber is thus ready for use. Its chemical characteristics are as follows:

Reaction:	Neutral
Ash-----	Per cent-- 7 to 10
Acetonic extract after 24 hours--do----	2 to 5
Chloroformic extract after 6 hours	do----- 13 to 20

From these figures it can be seen that the regenerated rubber possesses the characteristics of a high quality product. Used in mixtures this rubber gives products the physical characteristics of which are comparable to those of mixtures obtained by employing crude rubber.

As previously mentioned, the mode of operation may vary in its details without departing from the inventive idea. Thus with reference to the example above given, the preliminary treatment of the scrap with the swelling or solvent agent may take place in an open tank provided with a suitable agitator; instead of operating at room temperature, the tank or drum could be somewhat heated, for instance to 40° to 50° C., as a result shortening the period of treatment.

Furthermore, some other among the substances previously mentioned, or mixtures thereof in various proportions in relation to the weight of the scrap, could be used as swelling agents instead of naphtha, their proportion, however, being always very high. In such an event, the liquid employed for the recovery of the swelling agent should naturally also be selected accordingly. All of these details, as well as those accompanying the various steps of the method (concentration of the sodium hydrate or other devulcanizing agent used, temperature of the autoclave, etc.), may vary according to the kind of scrap used, and according to the possible advantage in using a given swelling or solvent agent, or a given devulcanizing agent, in preference to another; although said details can be easily determined in each particular case by a technician skilled in the art.

UMBERTO SARTORELLI.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF PAINTING COLORS

Hermann Staudinger, Freiburg I. Br., and Paul
Kümmel, Oranienburg, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed April 2, 1940

This invention relates to a process of improving the viscosity and luster of painting colors produced on the basis of drying oils or drying artificial resins, the term "drying" referring primarily to the absorption of oxygen from the air or from added oxygen suppliers while a firm film in the form of layers or coatings is being developed.

Layers or coatings formed of linseed oil, wood oil, artificial resin modified by such an oil, and the like are usually dull after production or subsequent drying, and the desired brilliancy can be imparted to them only by polishing or by subjecting them to similar treatment.

It is known to obtain layers and coatings showing a high polish immediately after production or drying by the use of suitable additions so that after-treatment may be dispensed with. For this purpose, it has been proposed to add to varnishes containing linseed oil, wood oil, stand oil, poppyseed oil, hemp oil, nut oil or mixtures of these oils zinc salts of benzoic or cinnamic acid or to form them in the mass from the free acids and zinc oxide. It has further been suggested to employ for the same purpose the aldehydes of the acids mentioned together with zinc oxide. By employing, in accordance with still another proposal, crotonic acid, acrylic acid, sorbic acid and similar unsaturated aliphatic acids the same effect as well as considerable ease of flow and uniformity of distribution can be attained whereby it becomes possible to add to the mixture increased amounts of pigments or substrates. This proposal is, however, open to the objection that such unsaturated aliphatic acids disclose highly unpleasant physiological effects, so much the more so as relatively large quantities thereof are required.

According to the invention, these drawbacks can be avoided to a very considerable extent by adding to painting colors of the class mentioned heterocyclic carboxylic acids which will improve the luster and viscosity thereof. Instead of these

acids the corresponding aldehydes may be used, though with somewhat less satisfactory results. It is remarkable that these acids combine low toxicity with great strength so that the amounts needed for addition are much smaller than in case of known substances.

For the purposes of the invention the carboxylic acids chiefly to be considered are furan carboxylic acid, which can be produced at very low cost, or its hydrogenation products, though other carboxylic acids may of course be used also, or these acids may be replaced by the corresponding aldehydes, i. e. furfurole, or corresponding aldehydes of other heterocyclic acids.

The following examples serve to illustrate the invention without, however, restricting it to this disclosure:

Example 1

To 100 parts by weight of a commercial stand oil-zinc white-enamel varnish one part of technically pure furan carboxylic acid is added.

The varnish thus produced shows very good flow and uniform spreading. After application of the paint and also after drying of the layer an excellent high polish is noticeable.

Instead of furan carboxylic acid the hydrogenation products thereof or another heterocyclic carboxylic acid may be used.

Example 2

To 100 parts by weight of a commercial synthetic resin-zinc white-enamel varnish on a glycerin-phthalic acid resin base modified during preparation by the incorporation of linseed oil 1.5 parts by weight furfurole or 1 part by weight furan carboxylic acid is added and worked in.

The effect produced is also very good, and the paints or coats are distinguished by great usefulness.

HERMANN STAUDINGER.
PAUL KÜMMEI.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF LATEX WITH LOW PROTEIN CONTENT

Gérard Eduard van Gils, Buitenzorg, Java, Dutch
East Indies; vested in the Alien Property Custodian

No Drawing. Application filed April 2, 1940

My invention relates to an improved process for the production of latex with a low protein content.

It is well known that the protein present in latex occurs therein partly in the serum and partly adsorbed on the rubber particles.

The part present in the serum is easily to be removed by repeatedly centrifuging or creaming the latex.

The other part, however, which is adsorbed by the rubber particles is so firmly united therewith that these proteins are carried along with the rubber with each centrifuging or creaming operation.

For this reason it is not possible either by repeated centrifugation or by repeated creaming to free the rubber from proteins below a certain content (see e.g. R.J.Noble I.R.I. Rubber Techn. Conf. May 1938, paper nr. 25).

The present invention makes the removal of the proteins on the rubber particles and the conveyance of this protein into the serum possible, so that the proteins may be removed from the latex by simple purification treatments e.g. by centrifugation or creaming operations. The characteristic feature of the invention is that for the removal of the proteins the principle of the adsorption displacement (exchange by adsorption) is used.

The latex which is preferably diluted before the treatment is contacted for the said purpose with a substance which is adsorbed by the rubber in a greater measure than the serum proteins. After a contact time of some hours, e.g. one night or more, the exchange equilibrium is established. A large part of the originally adsorbed proteins has then left the adsorption layer and is conveyed into the serum. Its place in the adsorption layer has now been taken by the capillary active substance mentioned above.

The dilution shows the following advantages:

1. The protein concentration is lowered and thereby the protein adsorption is weakened.

2. Better purification is possible, because of the greater difference of the rubber contents before and after the centrifugation.

As the protein displacing substance any substance can be used which is stronger adsorbed by rubber than the latex proteins.

Examples of suitable substances are soaps, such as sodium-, potassium- or ammonia salts of the higher fatty acids or naphthenic acids, sulfonated compounds, e.g. Igepon, sulfonated Lorol, Turkish Red oil etc. saponine and related substances, colloidal suspension of lipoids, fosfatids etc., and

generally all those substances which can be used as wetting agents, detergents, emulgators, stabilizers etc.

In connection with the centrifugation or creaming it be mentioned that in order to obtain as intensive a purification as possible latex must be used as far diluted as possible and an attempt should be made to obtain an as concentrated cream as possible. Therefore centrifugation is in this respect better than creaming.

The addition of soaps to latex before centrifugation has long been known. The object thereof was, however, exclusively an improvement of the mechanical stability of the latex (Noble "Latex in Industry", page 130). In creaming processes soaps have also sometimes been used, as it has appeared that by the viscosity decreasing action of soap the creaming is improved (Archief voor de Rubbercultuur 23, 1939, Page 14 "Viscositeit en Oproomingscapaciteit van Latex", British Specification 413,185 Netherlands Patent Nr.39, 122).

In the process according to the invention the function of the soap is, however, quite different i.e. the function is that of adsorption displacer.

The fact that the process is quite different clearly appears from the fact that the displacement of the proteins from the adsorption layer requires some time. If the centrifugation is effected directly or shortly after the addition of the soap the adsorbed proteins are not removed. This only occurs when after the soap addition the latex is kept into contact with the soap for some time e.g. at least one night (vide Example 3).

By the incorporation of soap the fatty acid or naphthenic acid content of the latex and the rubber prepared therefrom is increased. In the application of the centrifugation process for separating the rubber from the serum a large part of the fatty acid or the like is removed with the serum; the final product, however, still contains an increased fatty acid content. In rubber obtained by coagulation with acid a large part of the soaps used for displacing the proteins by adsorption is converted into the free acid.

It has now appeared that the amount of fatty acid or the like, especially of the free acids, can be decreased if the rubber sheets produced from the latex with low protein content are treated with a solution of an alkaline compound. Very suitable for this purpose are ammonia and also diluted alkali solutions.

When the coagulation has taken place by other means than the addition of acid and the fatty

or naphtenic acids or sulfonated compounds are still present in the rubber in soluble condition, the can also be removed therefrom with the aid of water or other solvents for the salts.

Preferably the still wet, preferably thin sheets are extracted in the alkaline liquid e.g. in diluted 0,5%-ic ammonia. The extraction period depends on the thickness of the sheets, the amount of fatty acid to be removed, the concentration of the extraction means, the temperature, etc. After an extraction during approximately 10 hours a decrease of the fatty acid content of about 40% was obtained. In many cases it is desirable to add anti-oxydants in order to improve the aging properties of the purified rubber.

The invention is further elucidated by the following examples

Example 1

This example shows that when before the centrifugation the latex is treated with ammonium oleate, the crepe prepared from the centrifuge cream has a lower nitrogen content than when the ammonium oleate treatment has not taken place.

As a starting product a latex was used with a dry rubber content (DRC) = 29,5% and a total solid content (T. S.) 32,6%. Nitrogen (N) — content of the crepe obtained in the usual manner after coagulation amounted to 0,52%.

A. A part of the latex was diluted with the 5-fold volume of water, to which 10 ml strong ammonia per l. was added.

B. Another part was diluted in the same manner with aqueous ammonia, in which, however, 0,5g ammonium oleate per l water was also added.

C. A third part was diluted in the same manner as B; here, however, the ammonium oleate concentration amounted to 1 g/l.

After having stood one night centrifugation took place.

	Per cent
A. Cream: DRC = 54,2%; TS = 54,4%; N-content crepe from cream-----	0,15
B. Cream: DRC = 50,4%; TS = 50,5%; N-content crepe from cream-----	0,12
C. Cream: DRC = 54,2%; TS = 54,4%; N-content crepe from cream-----	0,09

Before coagulation the cream was always diluted to a DRC of about 10%.

Example 2

Quite analogous to example 1 with this difference that instead of ammonium oleate the soap has been used traded under the trade mark "Sunlight" in the concentration of 1 g per l diluted latex.

Starting latex: DRC=32,6% TS=35,5%.

Mixed: 800 cc of latex + 5,5 l water + 60 cc of ammonia.

Centrifuged this gives a cream with DRC = 49,8% and from this a crepe was prepared with a N-content of 0,14%.

The same experiment, however, with addition of soap to the diluting water gave after having stood one night and centrifugation a cream with DRC = 52,2% and from this cream a crepe could be prepared with a N-content of 0,09%.

Example 3

Herein it is shown that it is essential to contact the latex for some time with soap because

the adsorption displacement is a process, demanding time.

Starting latex DRC = 27,5%; TS = 23,9%.

Crepe prepared herefrom N = 0,52%; Aceton extract = 2,76%.

The following mixture was prepared:

latex -----	l--	4
ammonia -----	ml--	30
ammonium stearate-----	g--	30
water -----	l--	12

(As ammonium stearate dissolves poorly, this substance had to be mixed beforehand with a little hot water).

A. Directly after the mixing a part was separated and centrifuged. A cream was obtained with a DRC of 55,8% from which a cream could be prepared with N-content of 0,13%; i. e. consequently not particularly low.

B. The remainder of the mixture was kept till the following day and then centrifuged. The cream had a DRC of 56,1% and herefrom a crepe was prepared with a N-content of 0,10%.

Example 4

1 l of latex was mixed with 4 l of water to which 10g Igepon had been added. After 24 hours the diluted latex was centrifuged in a Laval-separator, and the cream so obtained was diluted and then coagulated. The coagulum was worked up to crepe and the nitrogen content was determined and appeared to be 0,09%.

Example 5

1 l of latex was mixed with 4 l of water to which 10g Turkish red oil had been added. After 24 hours the diluted latex was centrifuged in a Laval-separator and the cream so obtained was diluted and then coagulated. The coagulum was worked up to crepe and the nitrogen content was determined and appeared to be 0,11%.

Example 6

1 l of latex was mixed with 4 l. of water to which 10g Lecithine had been added. After 24 hours the diluted latex was centrifuged in a Laval-separator and the cream so obtained was diluted and then coagulated. The coagulum was worked up to crepe and the nitrogen content was determined and appeared to be 0,10%.

Example 7

In this example it is shown that by starting from a cream purified already by a single centrifugation (without soap treatment) diluting this cream, treating with soap and centrifuging again, from the second cream a crepe can be prepared with very low nitrogen content.

A. A cream obtained by centrifuging of ammoniated latex was diluted to a DRC = 5%, treated with "Sunlight"-soap in a concentration of 2g per 1 l mixture. After having stood and being centrifuged a cream was obtained with a DRC of 29,9% and herefrom a crepe with a N-content of 0,03%.

B. Remainders of centrifuge cream were collected, diluted to a DRC of about 7%, treated with ammonium stearate in a concentration of 1 g/l diluted latex. After centrifuging again a cream was obtained with a DRC of 64% and herefrom a crepe could be prepared with a N-content of 0,05% and an ash content of 0,06%.

Example 8

Latex obtained according to any one of the preceding examples is coagulated and sheets of a thickness of 0.2 inch obtained from the protein-poor latex, in a still wet condition extracted in an aqueous alkaline solution, e. g. in 0.5% ammonia. After an extraction of several hours, 12 hours being a suitable time, the sheets are removed from the liquid and washed with pure water to remove traces of ammonia from the rubber.

The rubber obtained according to these examples has a very low protein content of below 0.12% N and preferably lower till below 0.03% N or even lower. As is well-known by the experts, a decrease of the protein content with relatively small amounts, such as e. g. 0.01% of N means an important improvement of the rubber, particularly for special purposes.

Rubber products according to the invention are particularly suitable for the production of coatings for electric cables, the water adsorbing capacity thereof being very low.

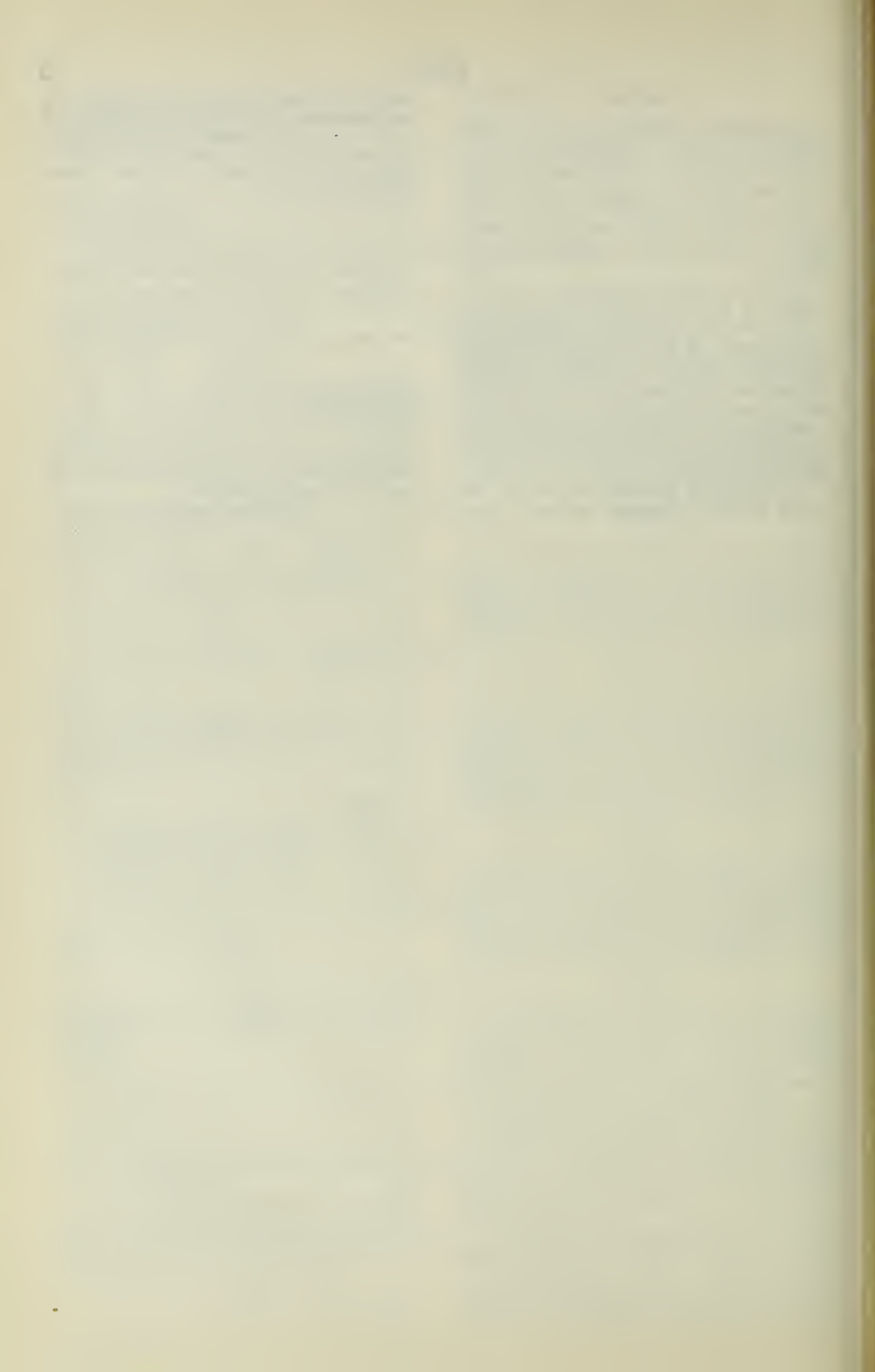
Of some crepes prepared according to previously mentioned examples, the water adsorb-

ing capacity was determined according to a method composed on the Proefstation West-Java at Buitenzorg. For comparison here also some data are given for a standard crepe and for a protein-poor crepe prepared from latex prepared with sodium-lye.

Sample	Ash	Nitrogen	Water adsorption (mg/100 cm ²) at 80° C			
			Raw rubber		Vulcanised rubber	
			7 hours	24 hours	7 hours	24 hours
Standard crepe.....	Per cent 0.19	Per cent 0.45	243	537	147	320
Crepe of example 3B....	0.07	0.10	63	137	62	120
Crepe of example 4B....	0.06	0.05	-----	-----	40	81
Crepe of latex treated with lye.....	0.11	0.09	60	121	58	112

By the term latex not only the common rubber is comprised but also gutta percha, balata and the like rubberlike substances.

GÉRARD EDUARD VAN GILS.



ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF HIGH POLYMERIC CONDENSATION PRODUCTS

Max Hagedorn, Dessau, and Ernst Schmitz-Hillebrecht, Bitterfeld, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 3, 1940

This invention relates to the production of high polymeric condensation products.

It is an object of this invention to produce high polymeric products by condensation.

Another object is the provision of high polymeric products of various properties.

These and other objects will be apparent from the following description.

It has been found that aromatic acids being substituted at least by two, if necessary substituted amino groups, may be condensed with aliphatic carboxylic acids or aromatic substituted aliphatic amino carboxylic acids. The condensation products thus obtained have a high softening point and good film-forming properties. The moulded products obtained therefrom show also good mechanical properties. The mixing proportion of the components leads to high polymeric compounds of a very wide range. If polyamino carboxylic acids are used as starting material in excess, preferably resinous glass-clear products are obtained. If the aliphatic amino carboxylic acid is in excess, preferably polymers of the so called superpolyamide type are obtained. Such condensates are not pure chain-polymerisates, but show also net- and bridge-formation.

The chemical and physical character of the high polymeric reaction products is extensively defined by the kind of aromatic polyamino carboxylic acids used in this reaction. The influence of the aliphatic amino carboxylic acids on the properties of the final product is within the scope of the facts known about superpolyamide resins. The application of the symmetrical 3,5-diamino benzoic acid for instance leads to very hard condensates, whereas the application of the 2,5-diamino benzoic acid results in softer high polymers.

As aliphatic amino carboxylic acids in principle all known compounds of this constitution may be used, preferably, however, ω -aminocarboxylic acids, containing 5 and more carbon atoms between the amino and the carboxyl group. Instead of the free aliphatic amino carboxylic acids just as well its condensable derivatives, like anhydrides, esters, nitriles, halides and the like may be employed. Instead of the purely aliphatic amino carboxylic acids also aromatic substituted ones may be applied. Care has to be taken, however, that the substitution does not occur on the primary amino group, as amino carboxylic acids with a secondary amino group react much slower.

It is also possible to use instead of the amino carboxylic acid mixtures of dicarboxylic acids and terminal diamines, which simultaneously are condensed amongst themselves into acid amides,

which afterwards react with the polyamino carboxylic acids.

Amongst the aromatic polyamino carboxylic acids preferably may be mentioned the various diamino benzoic acids, diamino naphtoic acids and the corresponding triamino carboxylic acids, in which still other places of the rings or an amino group may be substituted.

Also such aromatic polyamides may be applied according to our invention which contain more than one carboxyl group, e. g. the 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid or diamino-diphenylmethane - 4,4'-dicarboxylic-acid-p-amino-diphenyl-aspartic acid.

The union of the various amino carboxylic acids is accomplished in the simplest form by melting, which may be done in the presence or absence of an indifferent solvent or non-solvent for the starting components or for the reaction product. The reaction temperature lies at an average within 175-250° C. If polymerization of the reactants into high molecular reaction products occurs already below that temperature range, this takes place very slowly and often without to obtain the maximal chain-length.

High purity of the starting materials and also the exclusion of atmospheric oxygen during the reaction is most important for the quality of the high molecular final product. The pressure in the reaction vessel is far less important. One may work at the normal atmospheric pressure, but also in a vacuum or with excess pressure, according to the steam- and sublimation pressure of the reactants and the kind of reaction-polymerization and/or condensation, whereby water is split off.

Generally it is not necessary to add special catalysts accelerating the polymerization. Most probably the polycarboxylic acid is already enough reaction accelerating. However, if the speed of the reaction is slow, it may be increased by catalysts. The number of catalytically effective substances is great corresponding to the variety of the reaction possibilities. Catalysts of an acid nature are most effective. There may be mentioned inorganic acids i. e. hydrochloric acid, aliphatic and aromatic carboxylic acids, phenols, sulfo acids, hydrohalides of amines or amino carboxylic acids, generally speaking compounds reacting under formation of organic acids. Secondly in this respect are indifferent neutral compounds like diatomaceous earth, active carbon, fuller's earth which essentially are surface active and basic compounds, preferably organic amines.

The field of application of the high polymers is very wide. Besides their usefulness for textile

purposes in the form of filaments they are well suited for the production of films (for photographic and other purposes), plates (as substitutes for glass), sheets or foils (for electric insulation, coating foils for cigarette tips, wrapping foils, adhesive foils, light filters, patterns, stencils, supports for prints or the like), sound records (either those in which the sound track is cut mechanically into the support or is impressed therein without removal of material. (The Edison or the Berliner method)), masses for the reproduction and printing arts, masses for dye-casting and moulding by pressure (production of camera parts and casings for rollfilm or film-packs by pressing or rolling, production of spools or parts thereof for photographic rollfilms by the moulding method), as adhesive or intermediate layers for composite glass. The sheets or foils made from the materials according to this invention may be provided with a metallic coating according to a known process.

The application of the products in form of films, filaments and the like takes place according to known processes: dye-casting, casting from the melt or from solutions, drawing from the molten mass or under pressure below the softening point, warm- and cold stretching, rolling, in order to effect an orientation of the molecules in one or several directions, etc.

Example I

ϵ -aminocapro lactam and 3,5 diamino benzoic acid, both purified by repeated crysallization, are well mixed and heated 20 hours at 200°C in a glass tube in a pure CO₂ atmosphere under quicksilver cover allowing an excess pressure of about 50 mm Hg.

The following variations may be mentioned:

- (a) 3 parts ϵ -aminocapro lactam + 17 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, red-brown, clear transparent.
- (b) 9 parts ϵ -aminocapro lactam + 11 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, red-brown, clear transparent.
- (c) 13 parts ϵ -aminocapro lactam + 7 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, red-brown, clear transparent.
- (d) 15 parts ϵ -aminocapro lactam + 5 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, of honey-like color, transparent til opaque.
- (e) 19 parts ϵ -aminocapro lactam + 1 part 3,5-diamino benzoic acid, a resin, stringy in liquid state, opaque.

The hardness and the melting point increase from *a-e*, the latter being capable of being moulded at temperatures above 300°C only. *a* is capable of swelling in formic acid, *b* to *d* are dissolved therein and yield films from this solution, which are brittle except *e*. *a* is not soluble in 25 per cent hydrochloric acid, *b* to *e* are soluble therein, partly also in acids of lower concentration.

Example II

ϵ -aminocapro lactam is condensed with 1,2-phenylene-diamine-4-carboxylic acid according to Example I as dihydrochloride at 190°C for 24 hours.

The following variations may be mentioned:

- (a) 8 parts ϵ -aminocapro lactam + 12 parts 1,2-

phenylenediamine-4-carboxylic acid, a resin, slightly sticky, bluish, clear transparent.

- (b) 12 parts ϵ -aminocapro lactam + 8 parts 1,2-phenylenediamine-4-carboxylic acid, a resin, slightly sticky, bluish, clear transparent.

- (c) 15 parts ϵ -aminocapro lactam + 5 parts 1,2-phenylene, diamine-4-carboxylic acid, a violet resin.

- (d) 19 parts ϵ -aminocapro lactam + 1 part 1,2-phenylenediamine-4-carboxylic acid.

a and *b* dissolved in formic acid yield a soft, slightly sticky film, the film from *c* is somewhat harder, the film from *d* is still harder.

Example III

ϵ -aminocapro lactam and 2,5-diaminobenzoic-acid-dihydrochloride are mixed and heated as in Example 1 and 2 at 190-210°C for 24 hours.

The following variations may be mentioned:

- (a) 8 parts ϵ -aminocapro lactam + 12 parts 2,5-diaminobenzoic-acid-dihydrochloride, a black-green, sticky condensate.

- (b) 12 parts ϵ -aminocapro lactam + 8 parts 2,5-diaminobenzoic-acid-dihydrochloride, a green, transparent resin, soluble in methanol.

- (c) 15 parts ϵ -aminocapro lactam + 5 parts 2,5-diaminobenzoic-acid-dihydrochloride, a green, transparent, sticky resin, soluble in methanol.

- (d) 19 parts ϵ -aminocapro lactam + 1 part 2,5-diaminobenzoic-acid-dihydrochloride, opaque, milky brownish resin of great hardness. It is insoluble in methanol, but dissolves readily in formic acid, m-cresol and concentrated sulfuric acid.

Example IV

4.5 grams ϵ -amino caproic acid, several times recrystallized are mixed with 0.5 gram 2,5-diaminobenzoic-acid-hydrochloride and heated at 200-205°C for 24 hours in a glass tube in pure CO₂ atmosphere under quicksilver cover allowing an excess pressure of about 50 mm Hg. A melt is obtained which is stringy in the liquid state, soluble in formic acid and which can be worked up from this solution into a mat brittle film.

If the reactants are mixed in the proportion 3.5:1.5 after heating for 48 hours, a dark colored melt is obtained soluble not only in formic acid, but also in hot water. The film from formic acid is transparent and brittle. If the reactants are mixed in the proportion 4:1 and a catalyst, e. g. ϵ -amino-caproic-acid-hydrochloride is added and the reaction mixture heated under the above mentioned conditions for 24 hours at 200-205°C, a dark-lustrous melt is obtained soluble in methanol and formic acid. After casting of this solution a sticky film is obtained.

Example V

3 parts hexamethylenediammonium adipate and 2 parts pure 3,5-diamino benzoic acid are caused to react at 200°C for 24 hours under conditions as mentioned in the preceding examples. A transparent, red color resin is obtained, not soluble in any solvent.

If the reactants are applied in the proportion 3:2, a transparent resin is obtained less red in color and capable of swelling in formic acid.

MAX HAGEDORN.

ERNST SCHMITZ-HILLEBRECHT.

ALIEN PROPERTY CUSTODIAN

REGENERATING OF VULCANIZED RUBBER

Walter Gumlich, Leverkusen-Schlebusch, and
Ruprecht Ecker, Köln-Rath, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed April 3, 1940

The present invention relates to improvements in the reclaiming of rubber vulcanizates and comprises a new method of renewing the plastic properties of vulcanized scrap.

Up to the present natural rubber is usually reclaimed by heating the vulcanizates with a highly concentrated caustic soda solution or with a solution of a mineral acid. The use of high temperatures and of softeners is often resorted to in order to produce a uniform and plastic reclaim, such processes being usually accompanied by material decreases in tensile strength. These processes generally require the application of high temperatures of about 180°C, the heating being continued for a prolonged time, say about 5-15 hours. Whereas processes of the character described are practically used for the reclaiming of natural rubber, there is still a lack of suitable reclaiming processes for synthetic rubber-like materials which are obtained by the polymerization of butadiene hydrocarbons or by the copolymerization of such butadienes with other polymerizable substances. The problem of reclaiming such synthetic rubber-like materials is the more grave as the vulcanizates are often built up from a mixture of natural and synthetic rubber and as the presence therein of a preponderant amount of synthetic rubber prevents the products from being reclaimable.

It is the object of the present invention to develop a new process which allows one to effect the reclaiming of rubber at a lower temperature and more quickly than it was possible in accordance with the hitherto known methods. A second object of this invention resides in the developing of auxiliary agents which are suitable for the reclaiming of natural rubber as well as of synthetic rubber-like materials of the character described. Other objects will be apparent from the following description and claims.

It has been found that vulcanized rubber (either natural or synthetic) can be reclaimed by incorporating therewith an aromatic mercaptane, i. e. a compound of the formula $R\cdot SH$ wherein R stands for an aromatic radical, and heating the mixture to a high temperature of for instance about 130 to about 150°C. In accordance with a preferred method of working the heating is effected in an atmosphere containing oxygen at a higher pressure and concentration per cm^3 than it is normally found in the atmosphere. The oxygen may be applied in any desired manner for instance in the form of air or of agents yielding oxygen under the conditions of working. In general, the vulcanizates are

treated with the aromatic mercaptanes in the presence of air and steam under pressure. In practice the ground vulcanizates are mixed with the aromatic mercaptane and placed in an autoclave, air being pressed into the same so as to reach a pressure of several atmospheres (say about 2-6), the necessary temperature being generated by causing compressed steam to enter the autoclave so that an increase of pressure of several further atmospheres is effected. The aromatic mercaptanes can be incorporated within the vulcanizates either per se or with the aid of the usual rubber softeners such as "caoutchol".

Examples for suitable reclaiming agents are thiophenols, thiocresols, thionaphthols, thioxylols and thioanthracenes. In general, these reclaiming agents are employed in an amount of about 1 to about 5% of the vulcanizate. Additional softeners, if any, are likewise employed in an amount of about 5% of the vulcanizate.

The present invention allows one to convert vulcanized natural rubber into a plastic and vulcanizable condition in a much shorter time and at a considerably lower temperature than it was possible in accordance with the hitherto known methods. For giving an example, vulcanized natural rubber can be reclaimed by means of the auxiliary agents of the present invention 4 times as quickly than it would be reclaimed under the same conditions in the absence of aromatic mercaptanes. Synthetic rubber-like materials of the character described can easily be reclaimed in accordance with the present invention, the resulting products showing an excellent plasticity, and, if vulcanized, very often better mechanical properties than vulcanizates of regenerated natural rubber or the original vulcanizates of the synthetic rubber. Therefore, the present invention also allows one to reclaim a vulcanizate which has been built up from a mixture of synthetic rubber and natural rubber even if the former is present therein in a preponderant amount.

Examples for synthetic rubber-like materials which have been employed for the present reclaiming process are the products of the sodium polymerization of butadiene-1,3, furthermore, the products of the emulsion polymerization of butadiene-1,3-hydrocarbons either alone or in admixture with other polymerizable substances such as styrene, acrylic acid nitrile and unsaturated ketones such as vinyl methyl ketone. Furthermore, there may be mentioned the products of the polymerization of chloro-2-butadiene-1,3. As a matter of fact, the present process can be applied to unused rubber scrap as well as to mate-

rials which have undergone a long continued usage.

The present invention is illustrated by the following examples, without being restricted thereto, the parts being by weight:

Example 1

100 parts of a ground vulcanizate of natural rubber is mixed with 3 parts of β -thionaphthol. After a 1-2 hours heating to 130°C the product has been converted into a plastic vulcanizable state. After a several times passing through a refiner one obtains a soft plastic sheet which can be compounded with a fresh rubber mixture. With a similar result the β -thionaphthol can be replaced by an equal amount of m-thiocresol or of m-methoxythiophenol.

In case the heating is effected at an overpressure of air of 2 atmospheres and of additional 4 atmospheres of steam the same result is achieved after a much shorter heating of say about 20 minutes.

Example 2

100 parts of a ground vulcanizate of a synthetic rubber-like material which has been prepared by the emulsion polymerization of 75 parts of butadiene and 25 parts of styrene is mixed with 3 parts of β -thionaphthol. An excellently plastic and vulcanizable product is obtained after a 1½ hours heating to about 130°. The reclaiming process can be performed within about 1 hour in case an overpressure of 3 atmospheres of air and 2 further atmospheres of steam is applied.

Similar results can be obtained by replacing the β -thionaphthol by an equal amount of thicanthracenes or of thiocresols.

Example 3

A ground vulcanizate of a synthetic rubber,

which has been prepared by the emulsion polymerization of butadiene and vinyl methyl ketone in the proportion of 1:1, requires a 1 hours heating to 130° in the presence of 3% of m-methoxythiophenol for being converted into a plastic and vulcanizable product. Also in this case the reclaiming can be accelerated by effecting the process in the presence of compressed air and compressed stream.

Example 4

3 parts of β -thionaphthol are incorporated within 100 parts of a product of the conjoint emulsion polymerization of butadiene and acrylic acid nitrile in the proportion of 3:1, 5% of "cautchol" being employed for securing a better interpenetration of the rubber and the thionaphthol. The mixture is heated for about 1½ hours to 130°C at an overpressure of air of about 2 atmospheres in the presence of 4 further atmospheres of compressed steam. The resulting product shows a good plasticity and exhibits excellent mechanical properties if vulcanized again.

Example 5

Vulcanized scrap containing asbestos fibers can be reclaimed in the following manner: 100 parts of the scrap are mixed with 100 parts of benzene. 5 parts of β -thionaphthol are added thereto, preferably dissolved in benzene and the whole is heated to 150°C for 7-8 hours while constantly agitating and stirring the mixture. The resulting reclaim can be reused for the preparation of vulcanizates. Such vulcanizates containing asbestos fibers are employed in a large scale for the preparation of plates, stuffings and the like.

WALTER GUMLICH.
RUPRECHT ECKER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF ALCOHOLS OF THE ACETYLENE SERIES

Walter Reppe, Willi Schmidt, Hermann Spänig,
and Adolf Steinhöfer, Ludwigshafen-on-Rhine;
Germany; vested in the Alien Property Custodian

Application filed April 4, 1940

The present invention relates to a process for the production of alcohols of the acetylene series.

We have found that alkinols, i.e. alcohols of the acetylene series, may be obtained in an especially advantageous manner by causing to flow aldehydes or ketones in the liquid state, which term wherever used herein shall also include aldehydes and ketones in the dissolved state, together with an excess of acetylene through a reaction vessel charged with an acetylides of a heavy metal of the 1st and 2nd group of the periodic system or with such compounds of these metals as are capable of forming acetylides by reaction with acetylene, separating from the excess of acetylene leaving the reaction room the vaporous substances contained therein and recycling the acetylene into the reaction room.

The reaction may be carried out with aliphatic aldehydes of saturated or unsaturated nature, for example with formaldehyde, acetaldehyde or crotonaldehyde, and also with araliphatic or aromatic aldehydes, such as benzaldehyde. Suitable ketones are, for example, aliphatic ketones, such as acetone or methylethylketone, and hydroaromatic or araliphatic ketones, such as cyclohexanone or acetophenone.

As catalysts there may be used the acetylides of the heavy metals of the 1st and 2nd group of the periodic system and in particular the acetylides of metals of the Group I a of that system and of mercury, copper acetylide being the preferred catalyst. While the heavy metal acetylides may be prepared per se, it is also possible to allow them to be formed in the course of the reaction itself from heavy metal compounds capable of forming the acetylides. Such compounds are, for example, salts of the said heavy metals, for example, cupric phosphate and acetate, cuprous or cupric chloride, ammoniacal copper sulphate or silver nitrate or mercury chloride or mixtures of these salts, if necessary in the presence of compounds capable of binding acids. Such compounds are, for example, the salts of alkali and earth alkali metals and of magnesium with weak acids, for example, the formates, acetates, carbonates and bicarbonates. There may also be used earth alkali metal hydroxides, such as barium or calcium hydroxide, and other weakly basic substances, such as zinc oxide, zinc carbonate, alkali metal phosphates and silicates. Solutions or suspensions of these compounds may be used. The catalyst may, for example, be dispersed in the aldehyde or ketone as a powder or may be rigidly arranged in the form of small pieces or deposited on a carrier. As carriers

silica gel or another inert carrier may be used, for example aluminium oxide, Fuller's earth, aluminium silicate, active charcoal or coke.

Catalysts suitable in the present reaction may be obtained, for example, in the following way (parts by weight):

(1) 4.5 parts of 20 per cent aqueous ammonia are added to a solution of 2 parts of crystallized cupric chloride in 100 parts of water. Acetylene is led into the solution thus obtained at ordinary temperature while stirring for 50 minutes. The precipitated cupric acetylide is filtered off by suction and washed with water.

(2) A solution of 30 parts of cuprous chloride in 20 parts of 20 per cent aqueous ammonia solution is diluted with 2000 parts of water and acetylene is led in while stirring after the addition of 50 parts of fuller's earth. The resulting precipitate is washed with water.

(3) A mixture of 40 parts of cuprous chloride and 40 parts of basic magnesium carbonate is suspended, while stirring in a solution of 2 parts of silver nitrate in 150 parts of water, the suspension being treated with acetylene at 70° C until the original pale yellow color has been converted into a dark red-brown. The mixture of silver and copper acetylene compounds thus obtained may be used as such or after bringing it onto pumice stone.

It should be understood that other methods for preparing the catalysts may be used with the same results.

Among solvents and diluents adapted for the purpose of our present invention we may mention in particular water, alcohols, ethers or mixtures thereof and hydrocarbons. When starting from aldehydes or ketones which are liquid under the reaction conditions, the solvent or diluent may entirely be dispensed with. When reacting aldehydes we prefer to use a weakly acid or neutral reaction, while when starting from ketones the reaction liquid may as well be alkaline. Generally speaking the hydrogen ion concentration is advantageously kept between about pH=2.5 and pH=12, in order to avoid a splitting of the acetylene alcohols and the decomposition of the catalyst.

The reaction is carried out at elevated temperatures, preferably between about 60° and 160° C, temperatures between 90° and 140° C being the most suitable ones.

According to our invention the alcohols of the acetylene series may be prepared continuously or discontinuously. Thus, acetylene may be introduced into a reaction tower charged with the

catalyst from below and passed through a downward stream of liquid or dissolved aldehyde or ketone. The trickling method may be used with special advantage: The liquid or dissolved aldehyde or ketone, for example an aqueous solution of formaldehyde, is caused to trickle at say from 60 to 110° C over a catalyst rigidly arranged in the reaction tower while an excess of acetylene is led in at the bottom of the tower. Instead in countercurrent the acetylene may, however, be led in the same direction as the liquid aldehyde or ketone through the reaction room. Superatmospheric pressure of say, for example, from 2 to 20 atmospheres, and, instead of pure acetylene, dilute acetylene from any source, for example acetylene in dilution with hydrogen, carbon monoxide or carbon dioxide, methane or steam, may be employed.

The heat resulting in the highly exothermic reaction causes the aldehyde or ketone and/or the solvent used in dissolving the aldehyde or ketone to be partially evaporated. The vapor thus formed, the quantity of which is a function of the partial pressure at the reaction temperature, leaves the reaction vessel together with the unconverted acetylene. On cooling, the acetylene is freed from the vapors contained therein and is returned into the reaction vessel.

By the constant discharge of acetylene saturated with vapors, the temperature in the reaction vessel may be easily so controlled that, even in the case of high throughputs, reaction vessels of a very great inner diameter may be employed. This control of the temperature prevents the catalyst to be decomposed by overheating by the heat evolved in the reaction even in the middle of the reaction space where an outside cooling is not or but difficultly possible, and thus prevents the yield to be unfavorably affected. The degree of evaporation and the temperature in the reaction vessel depend on the quantity of the acetylene circulated through it. The solvent, the pressure and the speed of the acetylene are preferably so chosen that the temperature of the catalyst or the temperature in the neighbourhood of the catalyst does not considerably exceed 160° C; as stated above, it is preferable to keep the temperature within a range of from 90 to 140° C.

Depending on the reaction conditions, the nature of the initial materials and the catalyst, mono- or divalent alcohols of the acetylene series or mixtures thereof are obtained. From acetylene and formaldehyde there may thus be obtained either propargyl alcohol or butine-2-diol-1.4 or their mixtures. Such mixtures may easily be separated, whereupon the monohydric alcohols of the acetylene series, for example, the propargyl alcohol, may be returned into the reaction vessel, where it is wholly or partially converted into the dihydric alcohol. When the monohydric alcohol has a low boiling point, it may wholly or partially be removed by the acetylene gas from which it may be separated by condensation together with the solvent and initial material before the acetylene is led back into the reaction vessel.

One embodiment of the present invention will be more fully illustrated by way of the following Example for the preparation of butine-2-diol-1.4 from acetylene and aqueous formaldehyde by the

trickling method; it is to be understood, however, that our invention is not restricted to the said Example.

Example

A vertical pressure-tight tube of alloy steel of 400 millimeters inner diameter and 12000 millimeters length is charged with 1400 liters of silica gel on which copper oxide has been deposited. This catalyst is prepared by soaking the silica gel twice with a saturated solution of basic copper carbonate in concentrated aqueous ammonia, drying and heating the grains to 400° C. During the course of the reaction the copper oxide is converted into copper acetylide. 650 kilograms of a 30 per cent aqueous solution of formaldehyde, preheated to 50 to 60° C, are allowed to trickle down through the tube in the course of an hour, while 300 cubic meters of acetylene (measured at 0° C and 760 millimeters) are simultaneously led in at the top of the tube. The pressure in the tube amounts to 6 atmospheres. The unconverted acetylene is pumped round in a cycle and the acetylene consumed by the reaction is continuously replenished. After a short time a temperature of from 100° to 120° C is set up in the main reaction zone of the tube. The reaction mixture leaving the tower is passed through a pressure-tight separator, where the aqueous solution of butine-2-diol-1.4 is separated from the acetylene and vaporized substances which are led into a cooler where they are cooled down to 40° C. In a separator connected with the cooler about 120 kilograms of water are collected per hour containing some propargyl alcohol and methanol. From the aqueous solution of butine-2-diol-1.4 the pure butine-2-diol-1.4 may be isolated, for example, by evaporating the water. The yield amounts to 96 per cent (percentage with reference to the formaldehyde employed). The acetylene and, if desired, the propargyl alcohol are returned into the reaction tube.

The present invention will be further described with reference to the accompanying drawing which diagrammatically shows an apparatus suitable for use in carrying out the reaction in accordance with our present invention.

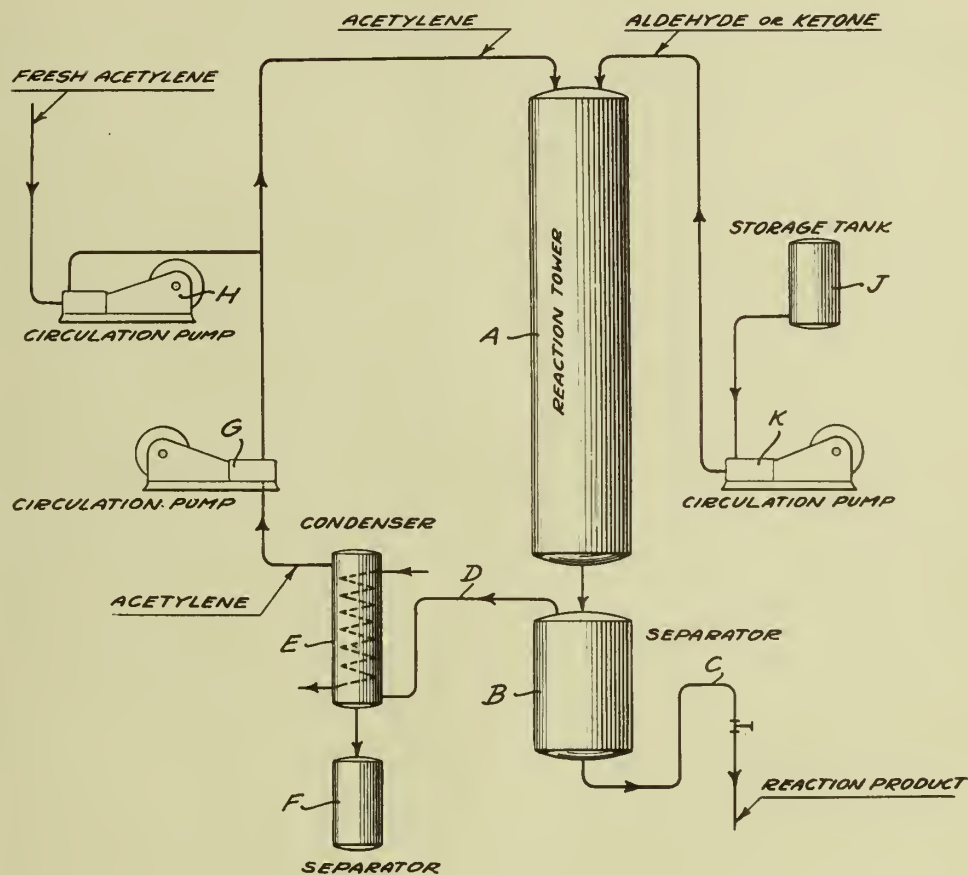
From the storage tank J the aqueous solution of formaldehyde is conveyed to the reaction tower A by pump K, while acetylene is simultaneously pumped in at the top of tower A. The bottom end of the tower communicates with a pressure tight separator B, where the liquid reaction product and the gas are separated. The aqueous solution of butine-diol is withdrawn through line C, whereas the acetylene and the steam (together with some methanol and propargyl alcohol) are passed to cooler E through line D. The water, methanol and propargyl alcohol are collected in separator F connected with the cooler E. The acetylene is passed to the circulating pump G and returned into the reaction tower. By the pump H fresh acetylene is pressed into the system at the rate at which it is used up during the reaction.

WALTER REPPE.
WILLI SCHMIDT.
HERMANN SPÄNIG.
ADOLF STEINHOFFER.

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W. REPPE ET AL
PROCESS FOR THE PRODUCTION OF ALCOHOLS
OF THE ACETYLENE SERIES
Filed April 4, 1940

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INVENTORS
Walter Reppe
Willi Schmidt
Hermann Spanig
Adolf Steinhöfer

BY
THEIR ATTORNEYS
Stue and Gordin



ALIEN PROPERTY CUSTODIAN

PROCESS OF RENDERING CASEIN SOLUBLE

Georg A. Krause, Munich 2 No, Germany; vested
in the Alien Property Custodian

Application filed April 4, 1940

The present invention refers to a process of rendering casein soluble by means of gaseous ammonia.

This method of making casein soluble implies a number of advantages, which to a part are due to the fact that the casein is only to a low degree charged with chemical substances. Whereas, for instance, in the manufacture of caseinate of sodium about 2 to 4 g. of sodium-hydroxide are required per 100 g. of dry casein, and even greater quantities in the case of hydrolysable sodium salts (carbonate, bicarbonate), about 0.6 g. of NH_3 are sufficient for the same quantity of casein, in order to prepare ammonia casein. NH_3 and the compounds resulting therefrom, respectively, are, moreover, not unrelated to casein, as are, on the contrary, the sodium compounds. When rendering the casein soluble by means of gaseous agents, it is furthermore unnecessary, to increase the quantity of liquids, which thereafter must again be expelled from the treated material, as would, contrary thereto, be necessary, if sodium salts are used for this treatment.

In spite of these preferences, the hitherto known processes of rendering casein soluble by means of gaseous ammonia, in which processes only dry casein was, moreover, used as initial material, failed due to the extremely long period of treatment, which was detrimental to the material treated, and also due to the difficulty of expelling the excess of gas retained by the casein of adsorption, in particular, however, due to the inequalities in gas absorption. Experiments of charging alcohol or ether with casein, and of subsequently treating the suspension or paste with gaseous agents, did not result in any improvement of the process, but made it more expensive due to higher costs of investment and manufacture. The technical difficulties implied in practising the process, were considered to be so enormous that since the time of the first proposals no serious effort or success has, hitherto, become known in this field in spite of repeated suggestions in literature.

The subject matter of the present invention is a process which offers a possibility of eliminating the difficulties hitherto experienced, when rendering casein soluble by means of gaseous ammonia. Tests furnished proof of the fact that the former unfavorable results are due to particular qualities adapted by the casein in the course of its treatment, because casein, if it is brought into contact with gaseous NH_3 , after a longer or shorter period corresponding to the humidity of the

casein forms on its surface a viscous layer of jelly, representing a saturated or super-saturated solution of ammonia in casein. This layer of jelly represents a stop preventing the direct absorption of the gaseous ammonia by the non-dissolved casein placed underneath it. Therefore this casein can only be supplied with dissolved ammonia from the layer of jelly enveloping it.

The diffusion of ammonia from the viscous jelly into the layer not yet influenced will, however, take place very slowly and in a perfectly uncontrolled manner. Supersaturated and saturated layers will adjoin others which have been left untreated, and the resulting finished material will consequently not be homogeneous.

It was considered almost impossible to expel the excess in NH_3 from the viscous jelly with ordinary means.

Under the present invention such phenomena are prevented by saturating under pressure the humid casein with the acting gas. In this manner the layer of material to be treated, which may have any desired height, appropriate to the individual requirements of the case concerned, will be permeated by the gas in a perfectly uniform manner, so as to be saturated with said gas within a comparatively short time, and in such a way that it is possible to increase and control the velocity of reaction in due correspondence to the pressure employed.

The saturation under pressure of the casein can be carried through in different ways. First of all it is possible to cause the gas, when in its compressed condition, to bring its influence to bear on the material to be treated, for instance in such a way that liquefied ammonia displays its influence by detention within a pressure-proof vessel. It is, however, also possible to proceed in such a way that the gas superimposed upon the material to be treated is exposed to pressure by means of mechanical influences, for instance in such a way that it is compressed by a piston, or that the gas, when exposed to normal pressure, is incorporated with the casein under pressure by means of a kneading or beating operation, or the like.

An embodiment of the invention, which is appropriate to the purpose in question, would also be represented by a combination of the aforescribed methods, i. e. by mechanically working the gas under pre-tension into the material to be treated, e. g. by equipping a pressure-proof vessel with a kneading device or an agitator, thus promoting the gas pressure by the mechanical process. In this manner it will be possible to par-

ticularly restrict the dimensions of the equipment necessary for treatment.

The solution of ammonia in casein will most probably commence to take place by way of the water contained in the material to be treated, even in case of these water contents being very small; as, on the other hand, the solubility of ammonia in water is a function of both pressure and temperature, different ways will be offered of controlling the process under the invention so, as to regulate it. It is, in particular, possible to control the concentration of the gas in the treated material by an alteration of the pressure, which latter, on its part, can be controlled by a change in temperature. On the other hand it would, however, also be possible, for instance to cool down the treated material also during the process of saturation; as otherwise the treated material would adopt a higher temperature during the course of the reaction process, it is thus possible to increase the concentration of the ammonia during the process of solution by cooling it, and by maintaining the pressure at the same height.

Finally it would also be possible to control the concentration of the gas by altering the water contents of the material to be treated, it also being possible, in doing so to combine the various aforementioned measures in any desired manner, if necessary.

In all of the embodiments it must be kept in mind that the process of rendering the casein soluble will take place in a solution of agents used for treatment, which is saturated in due correspondence to the pressure of the agent used for treatment and to the temperature existing, at the time, because the pressure above a liquid is always equal to the steam pressure, and to the aggregate amount of the partial pressures, respectively.

When availing oneself of the process under the present invention for practical operation, it is either possible to successively add the gas in stages up to the moment when solubility of the casein is attained, or contrary thereto at first to use an excess in gas and to again compensate such excess later on by an addition of untreated casein. It is preferable for this purpose to provide the equipment for treatment with a device making it possible to draw test quantities, in order to be able at any time to ascertain the condition of the treated material, and the completion of the treatment, respectively, it, however, being necessary to saturate the casein with the agent used for treatment in strict correspondence to the water contents, and in such a way that the pH figure can be controlled.

In case of an excess quantity of ammonia being present in the treated material after saturation, such excess can be expelled in an appropriate manner, and under certain circumstances can again be used for circulation. It is preferable for this purpose to heat the casein, e. g. in vacuo, and at the same time, or subsequent thereto, to suck off such gas as has been retained by adsorption. The ammonia excess can be reclaimed by having it adsorbed by cold water, from which it is then expelled and again re-introduced into the process under the present invention e. g. after its previous liquefaction.

A particular advantage will result in the treatment under the present invention of such casein as will be so treated after precipitation, washing, and after having been partly freed of water by mechanical means.

When proceeding in this manner, the equipment for drying the casein can be dispensed with, and the heat used for expelling the gas will expedite the drying process.

Though this is not absolutely necessary, the drying of the finished material, which has been treated, is preferably carried out in such a way that the casein is already dried in the course of expulsion of the superfluous treatment agent, this drying process in a preferable embodiment of the present invention taking place in such a way that saturation, removal of gas, and drying, are continuously taking place in one common vessel. For this purpose a vacuum-boiler can, for instance, be used, which is also resistant to pressure, and equipped with an agitator or a kneading device, and with an appropriate heating apparatus. Particular care must, however, be taken to carry out the expulsion of gas and the drying action in such a way that a large surface is exposed to the treatment, in particular, where casein with lower water contents than 70% is concerned, because the viscous jelly offers a high resistance both to the passage of heat and to the vacuo. If a great-surface thin-layer process on vacuum rollers or sheets in a vacuum drying cabinet, which could also be used for treatment, is not selected, and if it is intended to render the installation particularly small and efficient, it is preferable to use the above mentioned vacuum kneading device, which can be heated and is able to resist pressure, and by which always other surface of the treated material are feed to the heating surface, and again conveyed away, wherefore it is possible to expel and suck off the gas used for treatment, or the water.

The present invention finally also covers devices for practising the new process. As already explained, a treatment vessel which can be sealed so as to be gas-tight, possessing conduits for gas supply and evacuation, and provided with a heating and cooling device, is particularly suitable for the inventive purpose. Such installations can also be equipped with controlling devices, e. g. pressure gauges, thermometers, hygrometers, or the like, by which the supply of gas, the adjustment of the operation-temperature, the water contents etc., are, corresponding to the condition of operation prevailing at the time, automatically controlled.

The drawing diagrammatically illustrates a device for carrying into practice the process under the present invention.

Kneaders 5 on two shafts 3 and 4, which are coupled in an appropriate manner, rotate within the treatment vessel 1 which by means of a lid 2 can be closed so as to be airtight, and are driven by a motor 6. 7 designates the conduit provided for a heating and cooling device 8, whereas 9 is a device for drawing test quantities, 10 being a pressure gauge.

Container 1 can be supplied with liquefied ammonia from bottle 11 by means of a moveable conduit 12 and a pressure reduction valve 13 with pressure gauge 14, and through a gas meter 15.

On the other hand a vacuum pump 16 is, through a cooling pocket 17, which is intended to store the condensed product, connected with the treatment vessel 1 by a conduit 18.

The manner in which the described installation is used, can be seen from the following description of operation, given by way of example:

50 kg. of casein, which has been precipitated with muriatic acid and repeatedly washed, its

water contents being kept at 50% by mechanical means (pressing or centrifugation), are placed into the kneader 1. After lid 2 has been closed so as to be gas-tight, the kneading device is started by means of motor 6, whereupon, controlled by the measuring device 14, 15 10 about 150 g. of ammonia under a pressure of 6 atmosphere, are feed to vessel 1. At the same time by means of device 8, the material to be treated, which has increased its temperature in consequence of the reaction process taking place, is cooled down to about 15° Celsius. After a kneading action of about 30 minutes, during which the pressure will become lower in the course of progress of the reaction, several grams of the treated material are taken out from the vessel by means of device 9. By measuring the pH figure and, if necessary, by subjecting the drawn material to a solution test, it is ascertained whether the treatment is completed. The pH 20 figure will naturally be dependent upon the desired qualities of the finished material, and in the present example of operation will probably be about 6.0 to 6.3

During the following stage, in which the gas is expelled and drying takes place, the material

to be treated is heated up to 53° Celsius and kept at this temperature by means of device 8, which, for instance, can be provided with a hot-water circulation. By starting vacuum pump 16, a vacuum of about 100 mm. of mercury column is brought about in the interior of vessel 1. The quantity of gas, which has been retained by adsorption, if any, is sucked off and the treated material then dried.

10 The casein which now still contains about 5 to 6% of water, is then withdrawn from the installation, and can be subjected in the customary manner to a further process of disintegration.

The material prepared under this process is 15 a semi-translucent, hard and splintery substance which in the course of the drying operation will spontaneously detach from the drying surface, which, further on, can be easily ground, and is without any residues readily soluble in cold and 20 hot water. In accordance with its previous treatment and the quality of the primary material it will contain about 85-90% of high-quality protein which is highly digestible, i. e. an article which can be used both in the food industry, and 25 for technical purposes.

GEORG A. KRAUSE.

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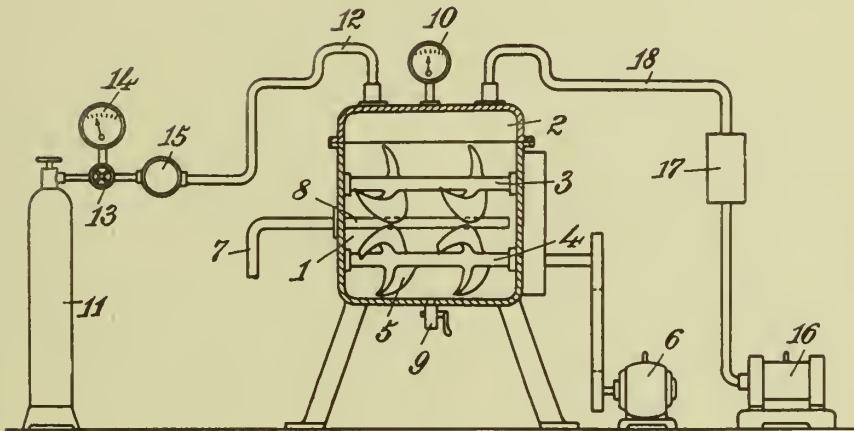
G. A. KRAUSE

PROCESS OF RENDERING CASEIN SOLUBLE

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Inventor :

G. A. Krause

By

Beau, Brooks, Buckley & Beau
ATTORNEYS



ALIEN PROPERTY CUSTODIAN

DYESTUFFS DERIVED FROM THE 2-AMINO-3-NAPHTHOIC ACID, THEIR METHOD OF MANUFACTURE AND THEIR APPLICATIONS

Georges Kopp and René Eugène Marcel Gangneux, Rouen, France; vested in the Alien Property Custodian

No Drawing. Application filed April 5, 1940

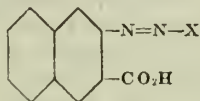
This invention relates to dyestuffs derived from the 2-amino-3-naphtoic acid, their method of manufacture and their applications.

While the anthranilic acid and its derivatives have been used frequently for the production of ortho-carboxy-ortho'-oxy- or -amino-azodyes for animal fibres, the 2-amino-3-naphtoic acid and its sulphonated derivatives have never been used for this application. The only technical dyestuffs which have been produced hitherto by means of the said products as diazotable bases have been dyestuffs for cellulosic fibres derived from the urea from the J-acid or dyestuffs for acetate rayon silks formed on the fibre.

Now, it has been found according to the present invention that azodyes of a great technical interest are obtained by diazotation of the 2-amino-3-naphtoic acid and its sulphonated derivatives and copulation in substance of the so obtained diazo compounds with copulation components copulating in ortho of a group NH^2 or OH with the exception of the derivatives of the 2-amino-5-naphtol-7-sulphonic acid. The so obtained dyestuffs can be converted in substance or on the fibre into metalliferous complexes.

The dyestuffs which form the subject matter of the present specification can be considered as falling into three categories:

1. Dyestuffs of the general formula:



(I)

in which X represents a copulating agent meeting the preceding definition and which may be, for example: an arylid of the acetylacetic acid, a betadiketone, a pyrazolone, a phenol, a naphthol, a benzenic diamine, a naphtylamine, an aminonaphtol and other similar compounds. These products are little or not soluble in wa-

ter; after their conversion—by means of the known general methods—into metalliferous complexes such as those of chromium, nickel, cobalt, iron or copper, they possess remarkable solubilities in organic solvents (other than pure hydrocarbons) and in cellulosic varnishes.

These metalliferous dyestuffs which are solid to light, to sublimation and to setting off, form a scale going from yellow-green to purple and brown. They give excellent results in the coloration of varnishes and paints as well as in the coloration in the mass or body of films and rayon silks on the basis of esterified cellulose.

II. Sulphonated derivatives of the dyestuffs of the above general formula "I".—These dyestuffs are well soluble in water and lend themselves to the various usual tinctorial methods. But their generally poor solidity to fulling does not permit to use them as such.

On the contrary, when dyes obtained by means of these products are subsequently treated with a polyvalent metal salt able to form complexes, the said dyes acquire a series of very interesting properties.

The scale of the so obtained shades goes from yellow-green to blue and brown. These products show a remarkable affinity for leather which they permit readily to dye in well united generally bright shades with a good yield.

Certain of them can also be used in the manufacture of lacquers through precipitation by means of alkaline-earth salts; these lacquers are solid to light.

It is to be noted that the use of the 2-3-amino-naphtoic acid and of its sulphonated derivatives in the above mentioned conditions permits to obtain, through copulation by means of the usual methods with the arylids of the acetylacetic acid, very greenish yellows which it was hitherto impossible to obtain in this category of dyes with so simple components.

The dyestuffs of this category can be obtained when starting from components containing sulphonic groups, or by sulphonation of dyestuffs corresponding to the formula "I".

III. *Metalliferous complexes of the dyestuffs of the above mentioned category "II".*—The dyestuffs of the category "II" can be converted into metalliferous complexes. The so obtained novel products and more particularly the chromiferous complexes are very interesting as well from the point of view of their shades and of their brightness as from the point of view of their general properties: unison, light, fulling.

Like the di-ortho-oxyazodyes (see The U. S. Patent 2,133,864 of the 12th Nov. 1934) the novel dyestuffs of the category "II" lead to two kinds of chromiferous products, the ones preferably being formed in a neutral medium and the others exclusively in a strongly acid medium.

The differences of properties between the complexes formed in a neutral medium (primary complexes) and the complexes formed in an acid medium are generally very strongly marked. In most cases the secondary complexes are brighter and unite very well on wool in an acid bath while the primary complexes unite badly.

Furthermore, the primary complexes require large quantities of acid and very long dyeing periods while the secondary complexes can be readily dyed by the usual methods; an advantage of the primary complexes lies, again, in their better yield when dyeing on wool in a strongly acid bath.

The production of the secondary compounds and their separation from the reaction media are generally very simple; it is sufficient, for example, to heat the dyestuff with a chromium salt in a diluted sulphuric medium. The secondary complex generally crystallizes from the reaction medium in the form of bright crystals. The acidity of the chromating media must be such that the pH is nearly 2. It is also possible to produce the primary complex intermediately and to continue the chromating operation after acidification of the mixture.

The formation of the primary or secondary complexes can take place in an open vessel or under pressure in presence or in the absence of organic solvents, of mineral or organic salts; it can be applied as well to the pure dyestuffs as to their mixtures, eventually with other dyestuffs than those which are defined in the present specification. It is also possible to produce mixed complexes containing a plurality of metals through a treatment by means of mixtures of metal salts able to form complexes.

The chromiferous complexes of the category "III" can be used either for dyeing or for printing animal fibres. These dyestuffs have a remarkable affinity for chrome-leather which they permit to dye in united bright shades of good solidity.

A certain number of these complexes are in the state of free acids soluble in organic solvents and can be used for the coloration of varnishes, films, pellicles and the like.

Finally, remarks similar to those made for the dyestuffs of the category "II" can be made with respect to the greenish yellows.

It is, moreover, possible to obtain dyestuffs of the category "III" by sulphonation of the metalliferous complexes of the dyestuffs of the general formula "I".

The following are various examples for the application of the invention:

EXAMPLE 1

187 parts of 2-amino-3-naphtoic acid are diazotized by means of 250 parts of hydrochloric

acid of 19° Be, 2000 parts of water, 138 parts of sodium nitrite in solution of 50% and the quantity of ice which is necessary for maintaining the temperature at +5° C. The so obtained diazo compound is poured in half an hour into the copulation bath prepared in the following manner:

177 parts of anilide of the acetylacetic acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda in solution of 35° Bé, 450 parts of crystallized sodium acetate are added and the whole is cooled to 0° C to the volume 4000.

The dyestuff, which gradually precipitates as its formation proceeds is separated in the usual manner. It appears in the form of a yellow powder which is almost insoluble in water, even in the state of sodium salt.

37,6 parts of the so obtained dyestuff are pacted in 250 parts of ethyl alcohol. A solution of chromium sulphate representing 7,8 parts of Cr_2O_3 in 25 parts of water and 5 parts of sulphuric acid of 36° Be is added.

The whole is then heated during 18 hours at 120° C in the autoclave. The so obtained product is treated with twice 500 parts of water in order to remove the chromium sulphate in excess.

The separated and dried dyestuff appears in the form of a yellow powder which is very soluble in organic solvents.

The applications of the solutions of this dyestuff in cellulosic varnishes give very bright greenish yellows or yellow greens which are solid to light and setting off.

EXAMPLE 2

To the diazo solution obtained according to example I a solution of 110 parts of resorcinol in 500 parts of cold water is added. Then the whole is poured during one hour into a solution of 180 parts of sodium carbonate. The so obtained dyestuff, which gradually precipitates as it is formed is separated in the usual manner.

30,8 parts of the so obtained dyestuff are pacted in 250 parts of ethyl alcohol. A solution of chromium sulphate representing 7,8 parts of Cr_2O_3 in 25 parts of water and 5 parts of sulphuric acid of 36° Be is added.

The whole is then heated during 12 hours at 120° C. in an autoclave. The crude formation is taken again with water and filtered. The so obtained precipitate is copiously washed in water in order to remove the chromium sulphate in excess.

The separated and dried dyestuff appears in the form of a brown powder which is soluble in organic solvents.

It tints the cellulosic varnishes in orange brown which is solid to light and setting off.

EXAMPLE 2 BIS

30,8 parts of the non-chromated dyestuff described in example 2 are treated with 400 parts of water at 90° and 12 parts of caustic soda of 35° Be. A solution of 14 parts of cobalt nitrate in 100 parts of water is added. The whole is maintained at 90° C. during half an hour and 15 parts of crystallisable acetic acid are added.

The so obtained dyestuff is soluble in organic solvents and in alcohol varnishes, which it permits to tint in brown yellow of good solidity.

EXAMPLE 3

The diazo solution obtained in the example 1

is poured into a solution obtained by dissolving 144 parts of bethanaphthol in 2000 parts of warm water and 115 parts of caustic soda in a solution of 35° Bé, by adding 180 parts of sodium carbonate and by cooling to 0° C.

The dyestuff, which precipitates as it is formed, is very little soluble in water.

When converted into a chromated complex in the same conditions as the dyestuff of example 1, it gives a brown black powder which is soluble in organic solvents.

The applications of the cellulosic varnishes tinted by means of this product are of a Bordeaux-red colour.

EXAMPLE 4

267 parts of 2-amino-3-naphto-sulphonic acid obtained by sulphonation by means of the sulphuric monohydrate of the 2-amino-3-naphtic acid are dissolved in 2000 parts of cold water by means of 345 parts of caustic soda of 35° Bé. 138 parts of a solution of sodium nitrite of 50% are added and the whole is ice-cooled to 0°. 600 parts of hydrochloric acid of 19° Bé are poured as rapidly as possible into this solution. The so obtained diazo compound immediately precipitates in the form of light yellow crystals which are absolutely insoluble in water. The whole is filtered in order to remove the salt matters and re-pasted in 1000 parts of water at 0°.

On the other hand, a solution of 189 parts of paratoluidide of the acetylacetic acid in 2000 parts of water by means of 115 parts of caustic soda of 35° Bé, is prepared and 300 parts of crystallized sodium acetate are added. This solution is cooled at 0°.

A solution of copulating agent is rapidly poured into the pasting of the diazo derivative. The formation of the dyestuff is very rapid. It takes a gelatinous form; the mass is stirred during two hours at a low temperature and heated during one hour to 70° C. The formation is then saturated by means of diluted hydrochloric acid up to a weakly purple reaction with "Congo". The dyestuff crystallizes in a very good form.

When separated, dried and converted into a sodium salt it appears in the form of a yellow-green powder. It dyes wool in yellow-green which after running through bichromate bath turns excessively little into another colour.

The dyes of this dyestuff when run through a bichromate bath are solid to friction, to alkaline fulling and to light.

EXAMPLE 5

In the preparation of the preceding dyestuff the paratoluidide of the acetylacetic acid is substituted by 201 parts of metaxyliide of the acetylacetic acid.

The so obtained dyestuff, which is a little deeper than the preceding one but of the same shade possesses a very strong affinity for chrome-leather which it dyes in very green yellow which is very deep in colour and of good solidity.

EXAMPLE 6

A diazo solution identical to the solution of example 1 is prepared and poured during half an hour into the copulation bath obtained in the following manner:

254 parts of 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are dissolved in 2000 parts of

water and 115 parts of a solution of caustic soda of 35° Bé. 45 gr. of crystallized sodium acetate are added and the whole is then cooled to 0° C.

The copulation is very rapid.

The so obtained dyestuff dyes wool by the bichromate method in orange yellow. The obtained dyes are solid to fulling and to light.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 7

A pasting of the diazo derivative used in example 4 is produced and a copulation bath obtained in the following manner is poured into this pasting:

174 parts of 1-phenyl-3-methyl-5-pyrazolone are dissolved in 2000 parts of water by means of 115 parts of a solution of caustic soda of 35° Bé. 450 parts of crystallized sodium acetate are added and the whole is ice-cooled to 0° C.

When the copulation is achieved a quantity of sulphuric acid of 36° Bé is added which is sufficient for causing the formation to become slightly acid with "Congo" red. The dyestuff which precipitates in an excellent form is thoroughly washed with a solution of sulphuric acid of 1% and can be considered as free from salt materials. When converted into a sodium salt through blending with carbonate, it dyes wool in orange yellow which is well united and solid to light and to alkaline fulling.

EXAMPLE 8

347 parts of 2-amino-3-naphto-disulphonic acid are dissolved in 4000 parts of boiling water. The solution is left to cool to the ordinary temperature and 150 parts of hydrochloric acid of 19° Bé are added. It is ice-cooled to 0° C. and 138 parts of a solution of sodium nitrite of 50% are poured during half an hour into this solution. The diazo derivative is entirely soluble in water. By a protracted stirring it crystallizes by and by.

The diazo compound is neutralized by the addition of crystallized sodium acetate up to a weak purple reaction with "Congo".

On the other hand a solution of copulating agent is prepared in the following manner: 207 parts of ortho-aniside of the acetylacetic acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda of 35° Bé. 300 parts of crystallized sodium acetate are still added and the whole is ice-cooled to 0° C.

The diazo compound is rapidly poured into this bath of copulating agent. The copulation is very rapid. The dyestuff precipitates partially. Sulphuric acid of 36° Bé is added up to a purple reaction with "Congo". The precipitation is complete.

When separated in the usual manner the dyestuff dyes animal fibres in yellow-green which after chromating has a good solidity to light and fulling.

EXAMPLE 9

In the production of the dyestuff of example 8 the orthoaniside of the acetylacetic acid is substituted by 174 parts of phenyl-methyl-pyrazolone. The so formed dyestuff is entirely dissolved. It is separated by acidification and salting out with sodium sulphate.

It dyes animal fibres in orange yellow which after chromating becomes solid to fulling and to light.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 10

A diazo derivative identical to that of example 4 is produced. The pasting is poured during one hour into a copulation bath obtained in the following manner: 110 parts of resorcinol are dissolved in 500 parts of cold water and 180 parts of sodium carbonate. The whole is then ice-cooled to 0°C.

The dyestuff, which precipitates partially, is separated by acidification with sulphuric acid.

It dyes wool in orange brown which after chromating turns to brown red. The obtained dyes are solid to washing, fulling and light.

EXAMPLE 11

In the production of the dyestuff of Example 6 the solution of the copulating agent is substituted by a solution obtained in the following manner:

247 parts of 2-naphtol-6-sulphonate of sodium are dissolved in 2000 parts of water, 180 parts of sodium carbonate are added and the whole is ice-cooled to 0°C.

The so obtained dyestuff dyes wool in bright crimson. After running through a bichromate bath the dye becomes bordeaux and has a good solidity.

EXAMPLE 12

A diazo derivative identical with that of Example 4 is produced. The pasting is poured during one hour into a copulation bath obtained in the following manner:

144 parts of beta-naphtol are dissolved in 2000 parts of water by means of 115 parts of caustic soda and 180 parts of sodium carbonate. The whole is then ice-cooled to 0°C.

The dyestuff which forms is separated in the usual manner and converted into a sodium salt; it dyes wool in bright red which through chromating turns to bordeaux. The obtained dyes are solid to light and fulling.

EXAMPLE 13

In the production of the dyestuff of Example 12 the beta-naphtol is substituted by 108 parts of paracresol. The so obtained product when separated through acidification dyes wool in yellow brown which through chromating turns to purple brown.

The obtained dyes have a remarkable solidity to fulling.

EXAMPLE 14

A pasting of a diazo derivative identical with that of Example 4 is produced. A solution of copulating agent prepared in the following manner is rapidly poured: 108 parts of metaphenylenediamine are dissolved in 2000 parts of water and 300 parts of crystallized sodium acetate are added.

The so obtained dyestuff dyes wool in bordeaux which through chromating turns to brown. The obtained dyes are solid to light.

EXAMPLE 15

A diazo derivative identical with that of Example 4 is produced. The pasting is poured in an hour into a copulation bath obtained in the

following manner: 224 parts of Neville-Winther acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda of 35° Bé. 180 parts of sodium carbonate are still added and the whole is ice-cooled to 0°.

The so obtained dyestuff when separated through acidification and salting out with sodium sulphate dyes wool in bright red which through chromating gives a bright reddish purple which is solid to light and fulling.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 16

A diazo derivative identical with that of Example 4 is produced and the pasting is rapidly poured into a copulation bath produced in the following manner: 143 parts of beta-naphtylamine are pasted during a few hours in 500 parts of water and 120 parts of hydrochloric acid of 19° Bé. 450 parts of crystallized sodium acetate are still added and the whole is ice-cooled to 0°C.

The dyestuff, which precipitates as it forms, dyes wool in crimson which after chromating turns to purple with good general solidities.

EXAMPLE 17

50 parts of the dyestuff of Example 3 are slowly introduced at the ordinary temperature into 500 parts of sulphuric monohydrate. The mixture is then heated during one hour to 50°C. and maintained at this temperature during one hour.

After this time the sulphonation is complete. The whole is left to cool to the ordinary temperature. It is then poured into 500 parts of ice. The dyestuff which first remains in solution precipitates and can be separated by filtration.

It appears in the form of a black powder which is soluble in water and sodium carbonate.

It dyes wool in red which turns to bordeaux through a treatment with bichromate.

EXAMPLE 18

A diazo derivative identical with that of Example 4 is produced and the pasting is poured into a copulation bath obtained in the following manner: 238 parts of 1-amino-8-oxynaphtalen-4-sulphonic acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda. 120 parts of sodium carbonate are still added and the whole is ice-cooled to 0°C.

The dyestuff partially precipitates during its formation. It is separated by salting out with sodium sulphate.

It dyes wool in bright red which through chromating gives a grey blue of good solidity.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 19

46.8 parts of the dyestuff produced in the Example 4 are pasted in 500 parts of water. A solution of chromium sulphate representing 7.8 parts of Cr²O³ in 25 parts of water and 10 parts of sulphuric acid of 36° Bé is then added.

The whole is then heated during 20 hours at 120-125°C. in the autoclave. The secondary chromated complex is entirely precipitated. After filtration it is converted into an alkaline salt by mixing with caustic soda in a sufficient quantity.

It dyes wool in an acid bath in yellow green solid to light and to fulling.

EXAMPLE 20

56,6 parts of the dyestuff produced in the Example 8 are dissolved in 1500 parts of boiling water. A solution of chromium sulphate representing 7,8 parts of Cr_2O_3 in 25 parts of water and 10 parts of sulphuric acid of 36° Bé is then added.

The whole is then heated with reflux during 12 hours. The dyestuff is first entirely converted into a primary chromated compound and then into a secondary complex which precipitates.

The obtained product appears in the form of a yellow green powder. It dyes wool in yellow green solid to light while perfectly preserving the natural and artificial cellulosic fibres.

EXAMPLE 21

45,3 parts of the dyestuff of example 7 are pasted in 500 parts of water. A solution of chromium sulphate representing 7,8 parts of Cr_2O_3 in 25 parts of water and 10 parts of sulphuric acid of 36° Bé. is then added. The whole is then heated at 115–120°C. during 12 hours in an autoclave.

After this time the secondary chromium dyestuff is entirely precipitated and there remains no trace of primary chromium compound.

It is to be noted that the dyestuff of example 7 is free from salt materials. The conversion into a secondary compound is complete. The conversion into an alkaline salt takes place as in example 18.

The obtained product dyes chrome-leather in bright orange, with a very high yield and of high brightness.

EXAMPLE 22

45,3 parts of the dyestuff of example 6 are dissolved in 1500 parts of boiling water. A solution of chromium sulphate representing 7,8 parts of Cr_2O_3 in 25 parts of water and 10 parts of sulphuric acid of 36° Bé. is then added. The whole is then heated with reflux during 20 hours.

After two hours heating the primary dyestuff is entirely formed and takes a very gelatinous form, then the secondary dyestuff forms.

The obtained product dyes wool in orange yellow solid to fulling and to light and of a good brightness.

The natural and artificial cellulosic fibres are perfectly well preserved.

The primary complex which has been formed intermediately can be separated by salting out. It dyes wool in an acid bath in yellowish orange which is less bright than the secondary dyestuff, but with a higher yield.

EXAMPLE 23

A solution of 50,2 parts of the dyestuff of example 14 in 1500 parts of water is heated during 10 hours with reflux with a solution of 15 parts of copper sulphate in 200 parts of water.

The copper compound, which has been precipitated by salting out, is separated. It dyes wool in bordeaux solid to light, preserving the natural and artificial cellulosic fibres in white.

EXAMPLE 24

10 parts of the dyestuff of example 1 are dissolved in 1000 parts of a cellulosic varnish on the

basis of nitro-cellulose. The dissolution is very rapid and the obtained solution is perfectly transparent. The applications of this varnish are of a deep yellow green colour solid to light and setting off.

EXAMPLE 25

2 parts of the dyestuff of example 4 are dissolved in 4000 parts of warm water and 5 parts of ammonium sulphate and 2 parts of acetic acid are added. 100 parts of wool are introduced at 50°C. The whole is manipulated during half an hour while heating to ebullition. 2 parts of sulphuric acid are still added and the ebullition is maintained further during half an hour.

The dyestuff dyes wool in very bright yellow green.

A bath of 1,5 parts of potassium bichromate and 2 parts of sulphuric acid in 1000 parts of water is prepared and heated at 60°C. The above mentioned dyed wool is introduced; it is heated up to ebullition and still manipulated during one hour at this temperature.

It is then copiously rinsed, dehydrated and dried.

The wool is then dyed in yellow green scarcely more red than the direct dye. The obtained dyes are solid to fulling and light.

EXAMPLE 26

100 parts of freshly neutralized chrome-leather are introduced into a fulling-mill containing 200 parts of water at 60° C. The fulling-mill is then set in motion. It is allowed to run a few minutes and through the hollow shaft of the mill $\frac{1}{3}$ of the solution obtained by dissolving 4 parts of the dyestuff of example 5 in 50 parts of water are added. The mill is then allowed to run during 15 minutes; the remainder of the dyestuff is added and the mill is allowed to run 25 to 30 minutes. The leather is put on the frame and the dye is achieved according to the usual technics.

The leather is dyed in very bright deep yellow green of good solidity.

EXAMPLE 27

2 parts of the dyestuff of example 22 are dissolved in 4000 parts of warm water; 5 parts of ammonium sulphate and 2 parts of sulphuric acid of 36° Bé. are added. 100 parts of wool are introduced at 50° C. It is heated to ebullition during half an hour and still manipulated at this temperature during one hour. The dye bath is very well exhausted. The wool is taken out, thoroughly rinsed, dehydrated and dried.

The wool is dyed in bright reddish purple of good solidity.

EXAMPLE 28

1 part of the dyestuff of example 11 is dissolved in 100 parts of water. 50 parts of barium sulphate and 10 parts of aluminum sulphate are added; the whole is heated to 50° C and a solution of 10 parts of crystallized barium chloride in 20 parts of warm water is poured into the mass. The latter is then heated to ebullition, filtered and washed. The so prepared bordeaux lacquer is solid to light and can be used for paints, graphic inks, colours for whitewashing and for wall papers.

The following table gives a summary of the properties of some dyestuffs produced according to the invention:

	Constitutions	Shade in varnishes	Shade on chrome-leather	Shade on wool	Shade on wool after chromating	Applications
1	2, amino-3-naphtic acid \longrightarrow acetoacetanilide (chromated).	Yellow green				Coloration of solvents, varnishes, plastic materials, rayon silks in the mass.
2	2, amino-3-naphtic acid \longrightarrow acetoacetyl-m-xylydine (chromated).	do.				Do.
3	2, amino-3-naphtic acid \longrightarrow phenyl - methyl - pyrazolone (chromated).	Orange yellow				Do.
4	2, amino-3-naphtic acid \longrightarrow resorcinol (chromated).	Brown red				Do.
5	2, amino-3-naphtic acid \longrightarrow betanaphthol (chromated).	Bordeaux				Do.
6	2, amino - 3 - naphto - sulphonic acid \longrightarrow acetoacetanilide.		Yellow green	Yellow green	Yellow green	Coloration of chrome-leather wool, pure or loaded lacquers.
7	2, amino-3-naphto-sulphonic acid \longrightarrow acetoacetyl-p-toluidine.		do.	do.	do.	Do.
8	Secondary chromated derivative of "7".		do.	do.		Do.
9	2, amino-3-naphto-sulphonic acid \longrightarrow acetoacetyl-p-cresidine.		do.	do.	Yellow green	Do.
10	2, amino-3-naphto-sulphonic acid \longrightarrow acetoacetyl - amino - hydroquinone-diethylether.		Clear yellow	Clear yellow	Clear yellow	Do.
11	2, amino-3-naphto-disulphonic acid \longrightarrow acetoacetanilide.		Yellow green	Yellow green	Yellow green	Do.
12	Secondary chromated derivative of "11".		do.	do.		Do.
13	2, amino-3-naphto-disulphonic acid \longrightarrow acetoacetyl-o-anisidine.		do.	do.	Yellow green	Do.
14	Secondary chromated compound of "13".		do.	do.		Do.
15	2, amino-3-naphto-disulphonic acid \longrightarrow acetoacetyl-m-xylydine.		do.	do.	Yellow green	Do.
16	2, amino-3-naphtic acid \longrightarrow sulpho-phenyl-methyl-pyrazolone.		Orange yellow	Clear yellow	Orange yellow	Do.
17	Secondary chromated compound of "16".		do.	Orange yellow		Do.
18	2, amino - 3 - naphto - sulphonic acid \longrightarrow phenyl-methyl-pyrazolone.		do.	Clear yellow	Orange yellow	Do.
19	Secondary chromated compound of "18".	Orange yellow	do.	Orange yellow		Coloration of varnishes, dyeing of chrome-leather, wool.
20	2, amino - 3 - naphto - sulphonic acid \longrightarrow 2' - chlorophenyl - methyl - pyrazolone-5' - sulphonic acid.		do.	Clear yellow	Orange yellow	Dyeing of wool and chrome leather.
21	Secondary chromated compound of "20".		do.	Orange yellow		Do.
22	2, amino - 3 - naphto - sulphonic acid \longrightarrow phenyl-methyl-pyrazolone.		do.	Clear yellow	Orange yellow	Do.
23	1, amino - 3 - naphto - sulphonic acid \longrightarrow resorcinol.		Brown red	Crimson	Brown red	Do.
24	Secondary chromated compound of "23".	Orange brown	do.	Brown red		Coloration of varnishes, dyeing of wool and chrome-leather.
25	2, amino - 3 - naphto - disulphonic acid \longrightarrow resorcinol.		do.	Crimson	Brown red	Dyeing of wool and chrome-leather, preparation of lacquers.
26	2, amino - 3 - naphto - sulphonic acid \longrightarrow p.cresol.		Purplish brown	Yellow brown	Purplish brown	Do.
27	2, amino-3-naphto-disulphonic acid \longrightarrow p.cresol.		do.	do.	do.	Do.
28	2, amino-3-naphtic acid \longrightarrow metaphenylen-diamine-sulphonic acid.		Brown	Red brown	Brown	Do.
29	2, amino - 3 - naphto - sulphonic acid \longrightarrow metaphenylen-diamine.		do.	do.	do.	Do.
30	2, amino - 3 - naphto - sulphonic acid \longrightarrow metaphenylen-diamine-sulphonic acid.		do.	Bordeaux	do.	Do.
31	2, amino-3-naphto-disulphonic acid \longrightarrow metaphenylen-diamine.		do.	Red brown	do.	Do.
32	2, amino-3-naphtic acid \longrightarrow 2, naphthol-6-sulphonate of sodium.		Bluish red	Crimson	Bordeaux	Do.
33	2, amino - 3 - naphto - sulphonic acid \longrightarrow beta-naphthol.		do.	do.	do.	Do.
34	2, amino-3-naphto-disulphonic acid \longrightarrow beta-naphthol.		do.	do.	do.	Do.
35	2, amino - 3 - naphto - sulphonic acid \longrightarrow Neville-Winter acid.		Purple	Red	Purple	Do.
36	Secondary chromated compound of "35".		do.	Purple		Do.
37	2, amino - 3 - naphto - sulphonic acid \longrightarrow S-acid.		Purplish blue	Bordeaux	Grey blue	Do.

GEORGES KOPP.
RENÉ EUGÈNE MARCEL GANGNEUX.

ALIEN PROPERTY CUSTODIAN

PROCESS OF CARRYING OUT ENDOTHERMIC TRANSFORMATIONS OF HYDROCARBONS

Heinrich Tramm, Muhlheim-Speldorf, Germany;
vested in the Alien Property Custodian

Application filed April 15, 1940

This invention relates to improvements in carrying out endothermic transformations of hydrocarbons by means of catalysers.

The transformation at elevated temperatures of hydrocarbons such as, for instance, the processes of aromatizing, dehydrating or splitting hydrocarbons by means of catalysts are generally connected with the separation of carbon the amount of which depends upon the extent of the transformation. The resulting coke precipitates upon the catalytic substances employed and makes them unserviceable. Therefore the precipitations must be burned out from time to time. For this purpose oxygenic gases, for instance air, may be passed through the reaction apparatuses (furnaces). The burning out of the precipitated coke takes place under considerable production of heat and increase of temperature. Considerable technical difficulties oppose themselves to the removal of the resulting heat, the more so because care must be taken to prevent excessive heating of the catalyser whereby the duration of life of the contact substances would be considerably diminished.

The heat produced by the burning-out of the coke may be removed through the walls of the apparatus, however this mode of working is only useful in connection with very narrow catalyst pipes and is useless for contact furnaces of large dimensions. On the other hand, it is possible to carry out the burning-out with large volumes of gases containing only a little oxygen so as to remove the resulting heat with the aid of the inert gases. Owing to the large quantities of gases required this method does not yield satisfactory results from a technical point of view.

Now I have found that these difficulties are avoided by regeneratively accumulating in the interior of the reaction apparatus the heat produced by burning out the coke. Hereby I obtain a considerable economic advantage because the regenerated heat may be utilized for supplying heat in the endothermic transformation of the hydrocarbon. By choosing a suitable ratio of the heat accumulating material to the catalytic material an excessive increase of heat during the burning-out operation can easily be avoided.

I am aware that the principles of regenerative accumulation of heat in the art of heating gases are well-known. In this connection also coke masses separated upon the accumulating brickwork were burnt at the same time. In the present case this step (which is well-known per se) is applied in an unprecedented manner to processes in which the separation of coke essentially

takes place upon the contact substances filled into the furnace. I ascertained the surprising fact that the burning-out heat is in a sufficiently rapid manner transmitted from the catalyst to the heat-accumulating brickwork, whence it is reflected during the subsequent reaction phase upon the heat-absorbing catalyst. By suitably alternating the reaction and the burning-out periods the temperatures of the catalyst may be kept within relatively narrow limits (for instance, between 470 and 490° C.) so that a deterioration of the contact material is not to be expected.

In the annexed drawing an apparatus for carrying out the invention is illustrated by way of example.

Fig. 1 is a horizontal cross-section on the line $x-y$ of Fig. 2 of a contact furnace constructed according to the invention;

Fig. 2 is a vertical cross-section on the line $a-b$ of Fig. 1.

1 denotes the mantle of a contact furnace constructed, for instance, in the form of a cylinder. This furnace is filled with ceramic plates 2, 3 placed cross-wise one above the other. From Fig. 2 it appears that a layer of plates 2 placed in a direction vertical to the paper is followed by a layer of plates 3 placed in parallel direction thereto. The plates 2, 3 consist of refractory ceramic material such as chamotte, sillimannit, porcelain, sintered corundum, magnesia stone or the like. Instead of ceramic material also other material, for instance, non-oxidizable metals such as chromium-nickel steel or the like may be used. The filling plates 2, 3 are about 4 inches high (h), 6 inches long (l) and about one third of an inch thick (d) (see Fig. 2). Any desired other dimensions may be used. The distance between the single plates should be as small as possible. In the modification shown in the drawing it may amount, for instance, to one third of an inch.

The interstices formed between the superimposed plates 2 and 3 are filled with the catalyst 4. The latter is prepared in a suitable form, for instance, in the form of balls, granules or filaments. A granulated catalyst with grains of from 1 to 3 millimeters has proved especially advantageous.

The hydrocarbons to be transformed are passed in gaseous form from the top or from the bottom through the contact furnace shown in Figs. 1 and 2. As soon as the corresponding separation of carbon has attained an excessive extent, the supply of hydrocarbon is stopped and the furnace is blown out with an inert gas (e. g. combustion gas). Thereupon oxygenic gases, for

instance, air is passed through the furnace. Under their influence a rapid combustion of the coke particles takes place. The developed heat is at once absorbed by the heat accumulating filling material. In the subsequent reaction period the accumulated heat is remitted to the catalyst which cools down owing to the endothermic character of the reaction.

In the process of aromatizing hydrocarbons the circumstances are such that the heat produced by the burning-out of the coke just suffices for covering the demand of heat necessitated by the reaction and the radiation of heat. Therefore the temperature of such a contact chamber can be kept constant within narrow limits (e. g. between 470 and 490° C.), provided that reaction and burning-out periods are properly alternated and the ratio of contact filling and heat accumulating material (about 60 to 65% ceramic material and 40 to 35% catalyst) is correctly chosen.

If in other processes (e. g. in dehydration processes) too much or too little heat is produced, no automatic equilibrium of temperature can be maintained inside the contact furnace, but the temperature must be controlled by external means. This may be effected in a well-known manner by flushing the reaction chamber before the beginning of the period of reaction for a reduced time with heat delivering or heat absorbing gases (e. g. waste gases).

Whether correction of temperature is used or not, the transformation of the hydrocarbons and the burning out of the coke must temporally fol-

low one after another in such a way that the contact furnace is subject to slight variations of temperature only. For instance, the endothermic catalytic transformation may be started at 490° C. and interrupted when the contact has cooled down to 470° C. Thereupon the burning-out operation, if desired with subsequent correction of the temperature, is effected in such a manner that the temperature of the furnace again rises to 490° C.

The annexed drawing shows a furnace the filling of which is formed by plates. Instead of these plates reaction furnaces filled with tubular or otherwise fashioned bricks may be used. The hollow spaces left free by the heat accumulating material are filled up with the fashioned contact material.

Also an irregularly introduced heat accumulating material may be employed. For instance, thickwalled so-called "Raschig rings" or single filling bodies may be used. Such fillings are introduced into the furnace at intervals, the granulated contact material occupying the interstices left free by the filling material.

Also with irregular configuration of the heat accumulating material the ratio of the accumulating material to the catalyst on the one hand and, on the other hand, of the reaction period to the burning-out period can easily be chosen in such a manner that inside the contact furnace only insignificant variations of temperature occur, for instance from 470 to 490° C.

HEINRICH TRAMM.

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H. TRAMM
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Fig. 2.

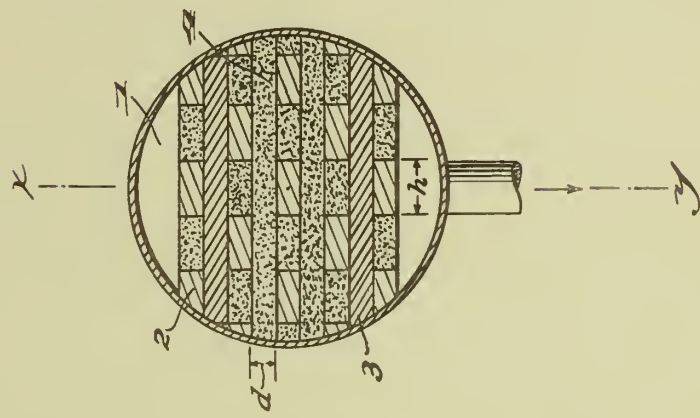
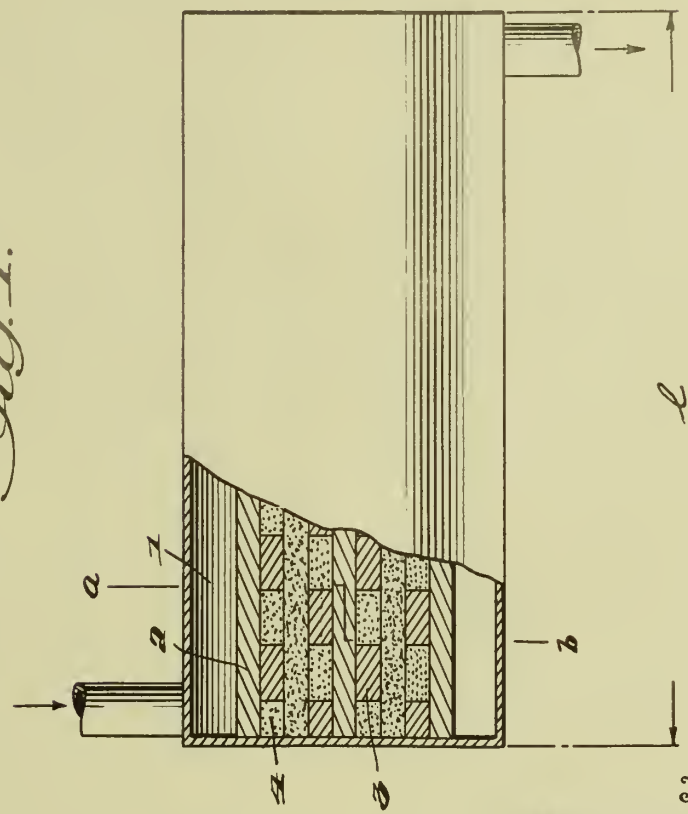


Fig. 1.



Inventor
 HEINRICH TRAMM,

By

F. P. Mc Intosh
 Attorney

ALIEN PROPERTY CUSTODIAN

CHEMICAL COMPOSITIONS

Hilger Peter Schmitz and Hermann Unterguggenberger, Munchen, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 16, 1940

This invention relates to a method of stabilizing emulsions of substances of high molecular weight. More particularly, it relates to stabilizing emulsions of resins against storage and transport conditions.

Emulsions, and particularly water-in-oil type emulsions of resins, such as, for example, alkyd resins, urea formaldehyde resins, etc., have come into general use because it has been found that the emulsified materials are capable of a wider range of uses than is possible using the same materials in the massive condition. However, these emulsions are frequently injured during shipment or storing by low temperature. When such emulsions are frozen and then melted again, they do not yield the original emulsion, but are broken to a certain extent, and this cannot always be corrected by stirring or other forms of mixing.

It is an object of this invention to improve the stability of emulsions of materials of high molecular weight. Another object of this invention is to improve the stability of water-in-oil type of emulsions containing resins, natural or synthetic, during storage and shipment. A further object is to improve the stability of such emulsions against freezing and resultant breaking. Another object is to improve the body and flowing characteristics of such emulsions. Other objects will appear hereinafter.

These objects are accomplished by the discovery that emulsions of materials of high molecular weight may be stabilized against conditions of storage and shipment, and particularly against low temperatures by the addition of neutral salts. The neutral salts also improve the body and flowing characteristics.

In order that the invention may be more fully understood, the following examples are set forth wherein Example I illustrates the prior art, and Example II illustrates the present invention.

Example I

A castor oil modified glyceryl phthalate resin was prepared by heating a mixture of

	Parts
Castor oil-----	155.9
98 per cent glycerol-----	117.0
Phthalic anhydride-----	204.6

under agitation at 200° C. until a test portion showed an acid number of approximately thirteen, which required about six hours of heating at 200° C. For storage purposes, the resulting resin was then cooled and diluted with an equal weight of xylene.

	Parts
Dilute resin as made above-----	50
Octyl alcohol-----	15
Xylene -----	40

were mixed to form a homogenous solution. To this solution was added, under vigorous stirring, a suspension, in water, of colloidal clay, of a particle size of 5 microns or less, the suspension consisting of

	Parts
Colloidal clay (dry basis)-----	2.4
Water -----	167.6

The resulting water-in-oil emulsion showed comparatively poor flowing properties, i. e., the emulsion did not flow down a glass rod in a continuous stream, but divided into relatively large aggregates.

A 25-gram sample of the above emulsion was placed in a test tube of 1-inch diameter and immersed for 15 minutes in a freezing bath consisting of solid carbon dioxide and acetone which cooled the sample to about -50° C. (50° below freezing) whereby the aqueous phase was frozen completely. The sample was removed from the freezing bath and allowed to warm to room temperature without stirring. The emulsion exhibited a curdy appearance and some clear liquid separated out and formed a layer at the bottom of the test tube.

Example II

A second emulsion was made by preparing a resin solution of exactly the same composition as used in Example I. To this solution was added, under vigorous stirring, enough of a suspension of colloidal clay in an aqueous solution of sodium chloride to produce an emulsion of substantially the same viscosity and the same total colloidal clay content. The amount of water used for this emulsification was 157.4 parts in which 10 parts of sodium chloride had been previously dissolved.

The emulsion thus produced could be poured in a continuous stream and exhibited excellent flowing properties, much superior to those of the emulsion of Example I.

A 25-gram sample of this emulsion was frozen to about -50° C. and thawed to room temperature using the same method and technique as in Example I. The salt-containing emulsion, after freezing and thawing, remained apparently unchanged and exhibited the same excellent flowing properties which it had before being subjected to freezing.

The emulsions with which this invention is concerned are emulsions containing materials of

high molecular weight, insoluble in water. The preferred materials are water-insoluble, natural and synthetic resins of the film-forming type, such, for example, as shellac, gum dammar, polymeric methacrylic acid derivatives, alkyd resins, phenol-formaldehyde condensation products, urea-formaldehyde resins of the type disclosed in U. S. Patent No. 2,019,865, and mixtures of said materials.

The preferred emulsions are water-in-oil emulsions. The oil phase may be any high boiling (140° C. to 200° C.) hydrocarbon of the aliphatic or aromatic type, such, for example, as the higher fractions of petroleum and coal tar distillations. In this oil phase is dissolved, or colloiddally dispersed, a water-insoluble resin of the type above described. The amount of resin present in the emulsion may, in general, vary from 1.5 per cent to 25 per cent of the total emulsion. Solvent-soluble plasticizers are preferably present, such, for example, as oil modified glyptal resins, drying oils, etc.

Any emulsifying agent may be used which is known to promote water-in-oil emulsion. Examples of these are solvent-soluble metallic soaps such as aluminum and magnesium salts of higher fatty acids, colloidal clay and those emulsifiers disclosed in U. S. Patent No. 1,603,155, patented October 12, 1926.

There may be included in the emulsions various modifying agents which improve their uses for

particular purposes, such, for example, as textile treating agents, pigments, and water-insoluble, solvent-soluble waxes.

The stabilizing agents which are within the scope of this invention are neutral salts, such, for example, as sodium chloride, potassium bromide, sodium sulfate. The preferred neutral salts are sodium and potassium halides, and especially preferred is sodium chloride. These agents are dissolved in the water phase of the emulsion. The water is, in general, present in an amount of from 20 per cent to 60 per cent of the total emulsion. Even slight amounts of the stabilizing agents have appreciable effect. In general, where only protection against freezing is desired, 0.5 per cent of the stabilizer is found to be satisfactory, although larger quantities may be used. Where improvement in the body and flowing characteristics of the emulsion is desired, the range is, in general, from 0.5 per cent to 20 per cent of neutral salt of stabilizer relative to water content, about 7 per cent of stabilizer being preferred.

The improved emulsions made according to the present invention may be used in the fabric treating art, the printing ink art, in the coating art, etc. They are characterized by improved stability at ordinary and freezing temperatures, and improved body and flowing characteristics.

HILGER PETER SCHMITZ.
HERMANN UNTERGUGGENBERGER.

ALIEN PROPERTY CUSTODIAN

PRECIPITATION OF EMULSION POLYMERIZATES

Richard Ludwig, Leverkusen-I. G. Werk, and
Helmut Meis, Marl Kreis Recklinghausen, Ger-
many; vested in the Alien Property Custodian

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The present invention relates to improvements in the emulsion polymerization of unsaturated compounds and in particular in the preparation of synthetic rubber-like materials.

The best hitherto known synthetic rubber-like materials are those prepared by the emulsion polymerization of butadiene hydrocarbons and particularly of mixtures of butadiene hydrocarbons and compounds containing an activated vinyl group, such as styrene, acrylic acid esters, acrylic acid nitril, the corresponding methacrylic acid derivatives or fumaric acid esters. The emulsion polymerization can be performed in an alkaline, neutral or acid medium. Suitable emulsifiers for the working in an alkaline medium are, for instance, alkyl-naphthalene sulfonic acids or soap forming fatty acids. On the other hand, the working in an acid medium requires the application of so-called "cationactive" emulsifiers such as mineral acid salts of higher fatty amines or of esters prepared from higher fatty acids and aminoalcohols. As a result of the emulsion process the polymeric products are obtained in form of a "latex" closely resembling that of natural rubber. Depending on the nature of the emulsifying agent the solids are precipitated from the emulsion in various ways. Thus, neutral reacting electrolytes can be employed in the case of a neutral or nearly neutral medium. Acids such as acetic acid have proved to be suitable for the precipitating of the solids from a strongly alkaline medium, the best results having been obtained by first precipitating such emulsions by means of neutral reacting water soluble salts such as sodium chloride and then rendering irreversible by the addition of acids the reversible precipitate thus obtained. From acid emulsions the solids can be precipitated for instance by means of alkaline reacting agents such as sodium carbonate or by means of alkali bisulfites and the like. The best suitable precipitating agents for the alkaline, neutral or acid emulsions, as the case may be, are partly described in literature and can in each case be easily determined by simple tests. Nevertheless the working up of such emulsions is connected with considerable difficulties chief among which is to be seen in the fact that the solids are often liable to stick together thus forming a strongly coherent cake the tough nature of which represents a serious obstacle for washing, purifying and drying operations. On the other hand, in the dry state the plasticity and softness of such polymerizates is inferior to that of natural rubber so that some difficulties are encountered in the uniting of the solids into a sheet of the kind made use of in the rubber industry.

Similar difficulties are encountered in the emulsion polymerization of such unsaturated compounds as yield other products than rubber-

like materials, though only part of such products is liable to stick together after the precipitation. On the other hand, there exists in every case the problem of effecting the precipitation in such a manner as to allow one completely to remove any impurities from the solids by washing operations. The removal of such impurities represents a serious problem in the preparation of such materials as it is evident from the fact that they are often employed for the preparation of transparent materials such as safety glass or electrical purposes.

It is the object of the present invention to do away with these difficulties and to develop a new process which allows one to precipitate the solids from such emulsions in a finely divided state in which they are not liable to stick together and can be led off through pipe lines together with the aqueous medium without inducing the danger of obstructions. Another object of our invention resides in the conducting of the precipitation process in such a manner that the solids can be easily purified by washing out. Still another object of our invention resides in the modifying of the individual precipitated particles in such a manner that they become sticky in any desired stage of the working up operations. In accordance with still another feature of this invention the becoming sticky is conducted in such a manner that the individual particles of the solids can be assembled into a coherent dry sheet without preventing the previous washing out and purifying operations. Still another object of our invention resides in the performing of such steps in a continuous manner, i. e. in a form which is particularly fit for the working in a technical scale. Other objects will be apparent from the following description.

Our invention in its simplest form comprises the performing of the precipitating step under such conditions that every unit of the emulsion is contacted with at least that amount of the precipitating agent which is necessary for effecting complete precipitation thereof, and in particular with an excess over the necessary amount. This can be accomplished for instance by pouring or dropping the emulsion slowly into or onto a solution of excess precipitating agent while stirring. In accordance with a preferred form of our invention a streaming emulsion of the character described is united with a streaming aqueous solution of excess precipitating agent. This procedure has proved to be very suitable for preventing any unit of the emulsion from being contacted with an insufficient amount of the precipitating agent, and at the same time allows one to conduct the precipitating step in a continuous manner. Both methods of working result in the formation of a finely divided precipitate which is not liable to stick together

and which is capable of being led off through gutters, channels, pipe line, and the like together with the liquid medium without giving rise to any agglomerations and obstructions. It is evident, that such properties of the precipitates which are obtained in accordance with our invention are doing a good share towards conducting the working up operations in a continuous manner.

Another feature of our invention resides in the discovery that the finely divided non-sticky particles thus obtained can be agglomerated by very simple manipulations. In the case of synthetic rubber-like materials of the character described this effect is best accomplished for instance by mixing the aqueous medium containing the solids with a multifold quantity of water. As such agglomeration is connected with and caused by an increase of the sticky character of the precipitate such operation must be applied at such a stage of the working up operations that no obstructions can occur any longer. In the case of a continuous precipitating process making use of a pipe line for the leading off of the precipitate together with the aqueous medium the addition of water is effected for instance shortly prior to or after the precipitate's leaving the pipe line. In consequence of the said agglomeration of the synthetic rubber the particles have assumed such a size that they are capable of being freed from the water by filtration. Therefore, our invention furthermore contemplates the passing of the agglomerated particles onto a filter for washing and purifying purposes. In accordance with a preferred form of working we are taking a continuously working filter such as an endless band filter or a revolving filter. In this manner the whole working up process beginning with the precipitating and ending with the drying can be performed in a continuous manner. An outstanding feature of our invention is to be seen in the fact that the agglomerated particles can be brought to a high degree of purity by irrigating the same with water while resting on the filter, and that on becoming dry they are liable to stick together thus forming a coherent rubber sheet of the type desired by the rubber factories. The removal of the water can be accelerated by mechanical means for instance by squeezing rollers or by the application of reduced pressure. It is preferred, however, to reduce the water content of the synthetic rubber-like material while being in contact with the filter not beyond the limit of about 50% in order to avoid undesirable obstructions of the meshes. The remaining water is best removed by leading the sheets through heating chambers it being to be understood that also these operations can be performed in a continuous manner.

The foregoing paragraph was concerned with the agglomerating purifying and uniting into a coherent sheet of synthetic rubber-like materials, it being to be understood that such operations are not restricted to rubber-like materials but can be applied also to such emulsion polymerizates as are suitable for other purposes than as substitute for rubber, always provided, however, that they show a sufficient liability to stick together. Such polymerizates are for instance those prepared from acrylic acid esters and vinyl esters or from mixtures of the same.

In the case of those emulsion polymerizates the precipitated particles of which are not liable to stick together, such products being for instance polystyrol or polyvinylchloride, the precipitating

process as described above allows one to free such precipitates from the last traces of any impurities though the uniting into a coherent sheet is impossible in those situations. The finely divided state of the precipitates obtained in accordance with the present invention prevents or at least diminishes the danger of impurities being occluded within the solids so as to be not removable by contact with water. On the other hand, such finely divided precipitates are also capable of being agglomerated so as to be converted into a state in which they can be washed out and separated from the aqueous medium by mechanical means, for instance, on the filter or in a centrifuge. Depending on the nature of the material the agglomerating can be performed either by the addition of water as it is more fully described above for the rubber-like materials or for instance by the application of a higher temperature. The necessary rise of temperature can be effected for instance by blowing in steam.

It has been disclosed in the foregoing paragraphs in which manner our new process can be performed. In the following we are giving some details regarding the necessary amount of precipitating agents for various emulsions and various precipitating agents it being to be understood that in other cases the nature and the requisite amount of the coagulants can be easily determined by tests and that the following figures can be employed for a discontinuous as well as for a continuous working. In the following table there are given the parts by volume of salt and/or acid solutions which have been found to be suitable for effecting complete precipitation of 50 parts by volume of a 30 per cent emulsion of various synthetic rubber-like polymerizates, the concentration of the salt solutions being in each case 8 per cent and of the acid solutions 1 per cent unless otherwise stated, and also the parts of water which are used for the agglomerating:

- | | |
|--|---|
| <p>(1) Mixed polymerizate of butadiene and styrol in the presence of alkylnaphthalene sulfonic acids and fatty acid salts as emulsifiers, the aqueous medium showing an alkaline reaction.</p> <p>(2) Mixed polymerizate as described sub 1 with the exception that the butadiene and the styrene are contained therein in the proportion of about 5.5 to 4.5.</p> <p>(3) A nearly neutral emulsion of a mixed polymerizate of butadiene and acrylic acid nitrile in the proportion of 3:1, the emulsifier being sodium alkylnaphthalene sulfonate.</p> <p>(4) An emulsion as described sub 3, the butadiene and the acrylic acid nitrile being in the proportion of 3:2.</p> <p>(5) An acid emulsion of the polymerizate described sub 1 in the presence of dodecylamine chlorohydrate.</p> | <p>90 parts of a sodium chloride solution and then 30 parts of an acetic acid solution and then 200 to 300 parts of water.</p> <p>(a) 120 parts of a sodium chloride solution and then 30 parts of an acetic acid solution.</p> <p>(b) 10 parts of a calcium chloride solution and then 30 parts of an acetic acid solution.</p> <p>(c) 20 parts of a magnesium chloride and then 30 parts of an acetic acid solution.</p> <p>(d) 40 parts of a potassium chloride and then 30 parts of an acetic acid solution.</p> <p>(a) 200 parts of a sodium acetate solution.</p> <p>(b) 20 parts of a calcium chloride solution.</p> <p>(c) 40 parts of an aluminum acetate solution and then 30 parts of an acetic acid solution.</p> <p>(a) 20 parts of a calcium chloride solution.</p> <p>(b) 20 parts of a magnesium chloride solution.</p> <p>50 parts of a 6 per cent sodium hydrosulfite solution.</p> |
|--|---|

It is to be understood that in each case the agglomerating can be effected by adding 200 parts of water to the precipitated emulsion.

As to styrene and similar starting materials for the preparation of materials other than those of a rubber-like character, the emulsion polymerization of such products can be performed for instance in the presence of sodium oleate, i.e. in an alkaline medium. In these cases formic acid can

be employed for the precipitating step. The amount of the same must be so chosen that the emulsion is rendered at least neutral or slightly acid. Thereupon we prefer to add ammonia to the precipitate so as to render it alkaline again. This step is taken in order to dissolve the oleic acid which has been precipitated

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together with the polystyrene, it being to be understood that no re-emulsification occurs thereby. The agglomeration can be performed by blowing in steam.

RICHARD LUDWIG.
HELMUT MEIS.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF CYCLIC OXYGEN COMPOUNDS

Willi Schmidt and Karl Seydel, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 19, 1940

This invention relates to the production of cyclic oxygen compounds and more particularly it concerns the production of alicyclic alcohols, ketones and phenols from alicyclic amino compounds containing six-membered carboxylic rings and one nitrogen atom, the rings being free from substituents other than those containing exclusively carbon and hydrogen atoms.

Cyclohexanol, cyclohexanone and their homologues and analogues in general are extremely valuable as solvents and as starting materials in organic processes. Methods are already known for the production of such alcohols and ketones involving the hydrogenation of phenols in the presence of catalysts.

The present invention is based upon the discovery that alicyclic alcohols, alicyclic ketones and also phenols may be prepared in highly satisfactory yields in a simple manner from nitrogenous starting materials, in particular from certain alicyclic amino compounds. By heating a compound of the type described above, for example cyclohexylamine, methylcyclohexylamine, dicyclohexylamine, phenylcyclohexylamine, decahydronaphthylamine, or mixtures thereof with a hydroxyl-containing compound, such as water or an alcohol, in the presence of a hydrogenation catalyst, alicyclic alcohols are formed together with ammonia or ammonia substituted by the radical of the hydroxyl-containing compound. Depending on the reaction conditions, these alcohols may be dehydrogenated to form alicyclic ketones or phenols.

In its broadest scope the invention involves heating cyclohexylamine, dicyclohexylamine or phenylcyclohexylamine or their homologues or analogues with a hydroxyl-containing compound in the presence of a hydrogenation catalyst. It is not necessary to carry out this reaction in the presence of hydrogen.

As catalysts there may be used in particular the metals of the 8th group of the Periodic Table, in particular the non-noble metals, or copper metal or oxidic or sulfidic hydrogenation catalysts. The preparation and the composition of these catalysts have extensively been studied and described in connection with the catalytic hydrogenation of aniline to form cyclohexylamine, with the production of alcohols from fatty acids or their esters or with the conversion of carboxylic acids, ammonia and hydrogen into amines or with the production of amines from carboxylic acid nitriles. These catalysts may be employed either alone or applied to the conventional carrier substances, such as pumice stone, aluminium oxide, fused silica gel and the like. It will be understood that the above given explanation of the catalysts is merely given for purposes of illustration and that the specific catalyst is not an essential part of our invention but that numerous modifications of these cata-

lysts may be made without departure from the spirit of our invention and that any other of the catalysts employed in hydrogenations of the type referred to above may be used.

The reaction according to our invention is preferably carried out under energetic conditions. The catalysts should be employed in a highly active state and the process is conducted preferably at temperatures ranging from 80° to 400° C. and in particular from 100° to 350° C. When working at temperatures exceeding 250° C, there may be formed cyclic ketones by dehydrogenation of the alicyclic alcohols primarily formed. The formation of such ketones may also take place to a substantial extent below 250° C. A substantial excess of the hydroxyl-containing compound over that required to substitute a hydroxyl group for a nitrogenous group, e. g. the amino group, for example from 2 to 50 times, should be employed. Suitable hydroxyl-containing compounds are in particular water, and also low molecular aliphatic alcohols, such as methanol, ethyl, propyl or butyl alcohol and the like. It is selfunderstood that higher alcohols may also be used but this does not involve economic advantages because too large a radical attached to the hydroxyl group simply constitutes a diluent decreasing the yield per unit of time and reaction space and slowing up the process.

The reaction may be carried out in the liquid phase or in the gas phase. It is possible to employ inert solvents for the reactants or inert diluent gases when working in the gas phase. Pressure, when employed, may be within the range of from 2 to 100 atmospheres, but higher pressures, such as 150, 200 or more may be employed.

The process may be conducted continuously for example by leading a vaporous mixture of cyclohexylamine and steam through a tube or a plurality of tubes charged with a hydrogenation catalyst. When working continuously in the liquid phase, the liquid mixture of cyclohexylamine and water or alcohol may be boiled under reflux or may be pressed through a vessel wherein the catalyst may be rigidly arranged. The liquid starting material may also be allowed to trickle over the catalyst while leading in counter-current a vaporized hydroxyl-containing compound of the kind defined above.

The actual temperature to be used depends on the activity of the catalyst and on the time of contact between the reaction mixture and the catalyst. In general, the time of contact should be long enough to ensure that the starting material introduced is at least partly subjected to cyclohexanol formation before leaving the catalyst. However, the temperature should not be so high and the time of contact should not be so long as to favor substantially the formation of aromatic

or alicyclic hydrocarbons which may occur under too energetic conditions.

Instead of cyclohexylamine or dicyclohexylamine or phenylcyclohexylamine or their homologues there may also be used mixtures of these compounds, for example the mixtures obtained in the hydrogenation of aniline or its homologues.

The following Examples serve to illustrate various modifications of our invention. It is, however, not restricted to these examples. The parts are by weight unless otherwise stated.

Example 1

Over a catalyst which contains 100 parts of nickel, 2 parts of chromium oxide, 1.5 parts of zinc oxide and 2 parts of barium oxide, which is deposited on pumice stone and which has been reduced in hydrogen at from 300 to 325° C there are led at 180° C the vapors of cyclohexylamine and water (ratio by weight 1:3) at a rate of 7 grams of cyclohexylamine per hour for one liter of the catalyst. The cyclohexylamine is completely converted under these conditions. The vapors emerging from the catalyst are condensed, the condensate is freed from water and then distilled. There is obtained for 4 parts of cyclohexanol containing cyclohexanone, 1 part of dicyclohexylamine.

This dicyclohexylamine may be added to fresh cyclohexylamine which is to be subjected to the conversion and thus also be converted into cyclohexanol. The yield of cyclohexanol may thus be increased to from 93 to 95 per cent of the amount calculated on the amount of cyclohexylamine used.

Example 2

Vaporized dicyclohexylamine and steam (ratio by weight 1:4) are led at 200° C over a catalyst as described in Example 1 at a rate of 8 grams of dicyclohexylamine per hour for 1 liter of the catalyst. The vapors emerging from the catalyst are condensed, the condensate freed from water and subjected to a fractional distillation. There are obtained small amounts of benzene and phenol, 60 per cent of a mixture of cyclohexanol and cyclohexanone boiling from 155 to 165° C and about 35 per cent of a mixture of dicyclohexylamine and phenylcyclohexylamine.

This mixture may be subjected again to the reaction with steam, whereby the yield of cyclohexanol (including the cyclohexanone formed therefrom by dehydrogenation) is increased to almost 90 per cent.

Example 3

Over a catalyst which has been used for some time for the conversion of dicyclohexylamine according to Example 2, there are led at 280° C a vaporous mixture of dicyclohexylamine and water (ratio by weight 1:5) at a rate corresponding to that used in Example 2. The condensate obtained is freed from water and then distilled. There are obtained 66 per cent of cyclohexanone containing small amounts of cyclohexanol, 3 per cent of phenol and 25 per cent of dicyclohexylamine containing a small amount of phenylcyclohexylamine.

Example 4

Over a reduced catalyst which contains 100 parts of copper, 1.4 parts of zinc oxide and 3 parts of barium oxide and which is deposited on pumice stone, there is led a vaporous mixture of cyclohexylamine and water (ratio by weight

1:3) at a rate corresponding to that used in Example 2. The condensate obtained is freed from water and distilled. There are obtained 71 per cent of cyclohexanone, containing 8 per cent of cyclohexanol, 7 per cent of phenol and 16 per cent of a mixture of dicyclohexylamine and phenylcyclohexylamine.

When carrying out the process at 340° C under otherwise identical conditions, there are obtained from the anhydrous condensate 33 per cent of cyclohexanone, 39 per cent of phenol and 21 per cent of a mixture of dicyclohexylamine and phenylcyclohexylamine.

Example 5

100 parts of cyclohexylamine, 100 parts of water and 10 parts of the pulverized and reduced catalyst described in Example 1 are boiled under reflux for 48 hours. There are obtained then 84 parts of cyclohexanol and 15 parts of amino compounds which may also be converted into cyclohexanol.

Example 6

Over 1000 cubic centimeters of reduced tungsten sulfide there are led per hour at 270° C 12 grams of a mixture of cyclohexylamine and steam (ratio by weight 1:3). By condensing the reaction gases and distilling the condensate, there are obtained for 100 parts of cyclohexylamine 70 parts of cyclohexanone, containing about 8 per cent of cyclohexanol, and 22 parts of a mixture of dicyclohexylamine and phenylcyclohexylamine.

Example 7

Over 100 cubic centimeters of a reduced zinc oxide-copper catalyst containing 2.4 parts of zinc oxide and 2.5 parts of barium oxide for each 100 parts of copper, there are led per hour at 330° C 12 grams of a vaporous mixture of cyclohexylamine and water (ratio by weight 1:3). By condensing the reaction gases and distilling the condensate, there are obtained for 100 parts of cyclohexylamine, 58 parts of cyclohexanone which contain 6 per cent of cyclohexanol, 5 parts of phenol and 27 parts of a mixture of dicyclohexylamine and phenylcyclohexylamine.

Example 8

25 cubic centimeters of a mixture consisting of 75 parts of butanol and 25 parts of cyclohexylamine per hour are vaporized and led at 200° C over 1000 cubic centimeters of the catalyst described in Example 1. The reaction gases are condensed. In the course of 36 hours there are thus obtained 119 grams of butanol, 173 grams of cyclohexanol, containing about 40 per cent of cyclohexanone, 54 grams of dibutylamine and 281 grams of tributylamine.

Example 9

10 parts of cyclohexylamine, 30 parts of methanol and 1 part of the reduced and pulverized catalyst described in Example 1 are charged in a pressure-tight vessel. 5 atmospheres of nitrogen are pressed in at normal temperature and the whole is slowly heated to 300° C, whereby the pressure is increased to 450 atmospheres. The reaction mixture is freed from the catalyst and distilled. Cyclohexanol, containing 7 per cent of cyclohexanone is obtained in good yields besides a mixture of cyclohexylamine and dicyclohexylamine.

WILLI SCHMIDT.
KARL SEYDEL.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE CONVERSION OF KETOXIMES INTO ACID AMIDES

Georg Wiest, Ludwigshafen-on-Rhine, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed April 19, 1940

The present invention relates to a process for the conversion of ketoximes into acid amides.

In the well-known Beckmann rearrangement of ketoximes at elevated temperatures, sulphuric acid of from 70 to 90 per cent strength is generally used. The presence of water is liable to assist undesired side-reactions, for example the dissociation of the oximes into ketones and hydroxylamine; higher percentages of water may also cause partial saponification of the acid amides formed in the rearrangement. Owing to the presence of aqueous sulphuric acid the process cannot be practiced in iron apparatus.

I have now found that the said side-reactions may practically be eliminated by carrying out the rearrangement with sulphuric acid containing at the utmost 2 per cent of water, i.e. sulphuric acid which is practically free or completely free from water, or oleum. The use of oleum is particularly advantageous if moist oximes are employed; the quantity and concentration of the oleum is then preferably so selected that the proportion of SO_3 contained therein will be sufficient to form sulphuric acid monohydrate with the water contained in the oximes. The oximes, as for example acetone oxime, methylnonylketone oxime, cyclohexanone oxime, methylcyclohexanone oxime, 1- and 2-oxodecahydronaphthalene oxime, may be dissolved in sulphuric acid of the said concentration range and run at temperatures of from 80° to 200°C , while stirring, into concentrated sulphuric acid which, as a diluent, assists the dissipation of the reaction heat. Instead of concentrated sulphuric acid, solutions having already undergone the reaction may also be employed as diluents.

The process is preferably carried out in a continuous manner while pumping the solution already rearranged in a cycle and continuously feeding to it fresh oxime solution or both oxime and sulphuric acid separately either at the same place or at different places. A corresponding quantity of rearranged solution is withdrawn from the cycle at another place. The reaction temperature most favorable for the rearrangement of the oxime used is adjusted by a proper proportioning of the oxime solution to be supplied and/or by outside cooling. The reaction temperature usually lies at between 100 and 150°C . For completing the rearrangement the solution may also be subjected to a subsequent heating if desired. The time of reaction, however, is usually very short, say a few minutes, so that high yields per unit of time and reaction

space are obtained. The process may be carried out in iron vessels.

Supplying the oxime and sulphuric acid to the cycle separately renders unnecessary the preparation of the oxime solution. To bring about rearrangement it will be sufficient to employ about $\frac{1}{2}$ to 1 mol of sulphuric acid per each mol of oxime, but larger proportions of sulphuric acid will do no harm either. As practically no undesired side-reactions occur in the process and, in particular, no splitting of the oxime nor saponification of the amide or the lactam formed takes place, the yields are excellent.

The following Examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said Examples. The parts are by weight.

Example 1

A solution of 550 parts of cyclohexanone oxime in 500 parts of sulphuric acid monohydrate is run into 500 parts of a solution of 1 mol of ϵ -caprolactam in 1 mol of sulphuric acid monohydrate at 140°C , while stirring vigorously, the said temperature being kept constant by cooling. After about 30 minutes, when the major part of the oxime has undergone the rearrangement, heating at 140°C is continued for another 10 to 15 minutes.

The solution, being faintly brown in color, is then run into 2500 parts of methanol at between 10 and 15°C while stirring. By leading in gaseous ammonia the sulphuric acid is precipitated as ammonium sulphate which is filtered off by suction and washed with methanol. The mother liquor and the methanol used for washing are united and evaporated. By distilling the crude product remaining behind the ϵ -caprolactam is obtained; after deduction of the amount of lactam added at the start, the yield is calculated to be 96 per cent of the theory.

The lactam may also be obtained by pouring the solution into aqueous caustic alkali solution while strongly cooling and extracting the aqueous solution with a suitable solvent, for example chloroform or ethylene chloride. The lactam may also be obtained by allowing the solution containing the reaction product to flow into milk of lime, filtering off by suction the calcium sulphate formed, evaporating the aqueous solution of the lactam and distilling the evaporation residue.

Example 2

280 parts of 98 per cent sulphuric acid are gradually run into a solution of 100 parts of ϵ -

caprolactam in 100 parts of sulphuric acid monohydrate at between 110° and 120° C, while stirring vigorously; at the same time 340 parts of cyclohexanone oxime are added and the reaction heat is carried off by outside cooling. When all of the oxime has been added, stirring is continued for 20 minutes at 120° C. The reaction mixture is then worked up in the manner indicated in Example 1. By distillation 408 parts of ϵ -caprolactam are obtained, i. e. 92 per cent of the theory.

Example 3

A solution of 50 parts of cyclohexanone oxime in 50 parts of sulphuric acid monohydrate is allowed to flow into 25 parts of sulphuric acid monohydrate at 110° C, while stirring vigorously, another 90 parts of cyclohexanone oxime being gradually added at from 130° to 140° C. Heating is continued at 130° C for another 30 minutes and the reaction product worked up in the manner indicated in Example 1, ϵ -caprolactam being obtained in a very good yield.

Example 4

115 parts of tert.-butylcyclohexanone oxime (melting point 135° C) are dissolved in 115 parts of sulphuric acid monohydrate; the solution is introduced, while stirring, into 60 parts of sulphuric acid monohydrate at between 80° and 90° C while cooling. The solution is further heated for a short time at 110° C, poured onto 500 parts of ice and neutralized with caustic soda solution of 35 per cent strength. The crystals precipitated are filtered off by suction, washed with water and dried. There are obtained 112 parts of the corresponding lactam (ter.-butyl- ϵ -caprolactam) which when recrystallized from ethyl acetate melts at from 157° to 158° C.

Example 5

60 parts of the oxime of cis-beta-oxodecahydronaphthalene are dissolved in 50 parts of sulphuric acid monohydrate and entered, while stirring, into 25 parts of sulphuric acid monohydrate at between 100 and 110° C. After working up in the manner indicated in Example 1, the crude product is distilled. There are thus obtained 56 parts of a mixture of the lactams of 1-amino-methylcyclohexyl-2-propionic acid and 1-beta-amino-ethylcyclohexyl-2-acetic acid which mixture melts at from 89° to 92° C and boils at from 154° to 155° C under a pressure of 0.5 millimeter mercury gauge.

Example 6

200 parts of 10 per cent oleum are gradually run into a solution of 50 parts of ϵ -caprolactam in 50 parts of sulphuric acid monohydrate, at between 70° and 90° C, while stirring, 210 parts of cyclohexanone oxime being introduced at the same time. The reaction being finished, heating is continued at 110° C for 15 minutes. The solution is then diluted with 600 parts of ice and neutralized with caustic soda solution of 35 per cent strength. The ϵ -caprolactam separates as an oily layer which contains about 34 per cent of water. The bottom layer is shaken with ethyl acetate; the residue remaining after evaporating the ethyl acetate is distilled together with the oily layer. There are obtained 250 parts of ϵ -caprolactam.

Instead of dry cyclohexanone oxime moist material, for example an oxime containing up to 10 or 15 per cent of water may be employed. In this case it is advantageous to use oleum of high SO₃-content in amounts sufficient for converting the water into about 100 per cent sulphuric acid.

GEORG WIEST.

ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING ARTIFICIAL SUBSTANCES FROM POLYVINYL COMPOUNDS

Hans Müller, Berlin-Wilmersdorf, and Ingeborg von Gizycki, Berlin-Nikolassee, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 1, 1940

This invention relates to a method of producing artificial substances from polyvinyl compounds.

To produce artificial substances from polyvinyl compounds, particularly from polyvinyl chloride, subsequently chlorinated polyvinyl chloride or vinyl chloride interpolymers, it has already been proposed to employ as softening agents such organic compounds which contain besides one or more aromatic groups, one or more aliphatic groups, each of which consists of a chain of at least 10 carbon atoms. These requirements are met, for instance, by the following softening agents: Homologous aromatic hydrocarbons with a highly molecular side-chain, esters of aromatic acids with highly molecular aliphatic alcohols, esters of aromatic alcohols or phenols with highly molecular fatty or oleic acids, aromatically substituted amides of highly molecular fatty or oleic acids and mixed ethers of aromatic alcohols and highly molecular aliphatic alcohols.

According to the invention, softening agents of the above-mentioned character are employed in which are present, instead of the aromatic group or groups, partly or wholly hydrogenized aromatic groups, heterocyclic groups and partly or wholly hydrogenized heterocyclic groups.

As instances for hydroaromatic compounds the

following may be mentioned: The esters of naphthenic acids with highly molecular fatty or oleic alcohols; cyclohexylstearate or tetrahydronaphthylaurate; lauric acid tetrahydronaphthylamide; the product resulting from the reaction of dodecylmagnesiumbromide on hexahydrobenzoic acid-nitril.

As instances for softening agents with heterocyclic groups the following may be mentioned: The product resulting from the reaction of highly molecular olefines with more than 10 carbon atoms on coumarone; furfurylpalmitate; the dodecylester of the pyromucic acid; lauric acid pyrimidylamide; the product resulting from the reaction of highly molecular fatty acid chlorides or highly molecular alkyl chlorides with more than 10 carbon atoms on carbazol or carbazol potassium.

The following softening agents with hydrogenized heterocyclic groups have proved particularly suitable: Tetrahydrofurfurylpalmitate; the keton obtained by the oxidation of the product resulting from the Grignard's reaction of tetrahydrofurfural on hexadecylmagnesiumbromide; stearic acid piperidide.

HANS MÜLLER.
INGEBORG VON GIZYCKI.

ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING ARTIFICIAL SUBSTANCES FROM POLYVINYL COM- POUNDS

Hans Müller, Berlin-Wilmersdorf, and Ingeborg
von Gizycki, Berlin - Nikolassee, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 1, 1940

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According to the invention instead of softening agents containing oxygen the corresponding sulphurous compounds are employed as softening agents. In lieu of the esters of phenol or aromatic alcohols with highly molecular fatty or

oleic acids already proposed as softening agents, the esters of thiophenol or aromatic mercaptans with highly molecular fatty or oleic acids, for instance, thiophenylstearate or the benzylmercapto-oleate are employed. Also the sulphur derivatives of the mixed ethers already proposed, i. e. sulphides which contain on the one hand an aromatic group and on the other hand a highly molecular aliphatic group, for instance, the phenyldodecylsulphide have proved particularly suitable.

Besides the homologous aromatic hydrocarbons in which the side-chain contains more than 10 carbon atoms, also another class of substances has given satisfactory results in which the side-chains and aromatic rings are linked by a direct C—C bond, i. e. aliphatic-aromatic ketones with an aliphatic chain of more than 10 carbon atoms. The product resulting from the Friedel-Crafts reaction of dodecylchloride on xylene and the undecylobiphenylketone may be cited as instances.

HANS MÜLLER.
INGEBORG VON GIZYCKI.

THE HISTORY OF THE

REIGN OF

CHARLES THE FIRST

BY

JOHN BURNET

OF THE UNIVERSITY OF OXFORD

IN TWO VOLUMES

THE SECOND VOLUME

CONTAINING

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CHARLES THE FIRST

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF HYDROXY-KETO COMPOUNDS HAVING A CYCLOPENTANOPOLYHYDROPHENANTHRENE NUCLEUS

Rupert Oppenauer, Amsterdam, The Netherlands;
vested in the Alien Property Custodian

No Drawing. Application filed May 1, 1940

This invention relates to manufacture of hydroxy-keto compounds having a cyclopentanopolyhydrophenanthrene nucleus; and it comprises a process in which an organic compound, containing a cyclopentanopolyhydrophenanthrene nucleus and having at least one keto and one non-tertiary hydroxy group attached thereto, is subjected to the action of a metal alcoholate in the presence of an inert solvent, whereby isomerization and/or dismutation takes place; all as more fully hereinafter set forth and as claimed.

This application is a continuation-in-part of my copending application, Serial No. 150,758, filed June 28, 1937. In this prior application I have described and claimed the same generic invention as that which is disclosed in the present application but in the present application the disclosure has been amplified by the inclusion of an additional specific example to which the claims are particularly directed.

The raw materials employed in the production of the 3-keto-17-hydroxy compounds having a cyclopentanopolyhydrophenanthrene nucleus, are usually the isomeric 3-hydroxy-17-keto compounds. Thus testosterone, which is a 3-keto-17-hydroxy compound, is usually prepared from dehydroandrosterone, which is a 3-hydroxy-17-keto compound. The 3-keto-17-hydroxy compounds, such as testosterone and dihydrotestosterone for example, not only have a greater activity than the isomeric 3-hydroxy-17-keto compounds but in addition they often show another physiological action, for example on the seminal vesicle and prostate.

The prior art methods which have been developed for the production of the 3-keto-17-hydroxy compounds from the isomeric 3-hydroxy-17-keto compounds or from natural starting materials containing such compounds have had the disadvantages that they are complicated and that the reactions employed do not produce the desired compounds directly but only via intermediate products, such as the hydroxy-esters, as described by Ruzicka, *Helv. Chim. Acta* 18, 1478 (1935), for example.

I have found that the desired compounds can be produced in a very simple and direct way by means of an isomerization reaction in which the raw materials are treated with lower molecular metal alcoholates in the presence of inert solvents. By this treatment there are formed not only the lower molecular alcohols derived from the alcoholate employed but also the alcoholates of the 3-hydroxy-17-keto compounds, the latter having the property, in the presence of an inert

solvent, of undergoing isomerization to form the desired 3-keto-17-hydroxy compounds with substantial yields which can then be recovered in the form of pure crystals. I have found that this isomerization reaction is applicable to all hydroxy-keto compounds having a cyclopentanopolyhydrophenanthrene nucleus in which it is theoretically possible for at least one of the hydroxyl groups to be replaced by or to exchange places with a keto group. This means that at least one of the hydroxyl groups must be non-tertiary. The hydroxyl and keto groups may be attached to one of the rings in the cyclopentanopolyhydrophenanthrene nucleus or to a side chain attached to said nucleus, for example in the 17 position. The more important compounds which are operative in my process are those containing at least one secondary hydroxyl group and in which the keto and hydroxyl groups are attached to different rings. By this method I have succeeded in converting the less active 3-hydroxy-17-keto compounds of the androsterone and dehydroandrosterone type into the more strongly active 3-keto-17-hydroxy compounds of the dihydrotestosterone and testosterone type, for example.

My process can be generally applied to the isomerization and dismutation of hydroxy-keto compounds of the types described and in which it is desired to convert these compounds into their isomeric hydroxy-keto compounds or into their polyalcoholic or polyketonic derivatives. My process is not limited to the use of the hydroxy-keto compounds in their pure state but crude or natural products, such as urine extracts, which contain hydroxy-keto compounds of the types defined are useful in my process. The reaction products and compounds obtained in this invention are useful as pharmaceuticals.

Various metal alcoholates can be used in the described process among which there can be mentioned sodium ethylate, aluminum isopropylate, chloro-magnesium-triphenylcarbinolate and tertiary aluminium butylate. The inert solvent employed should be a substance having no reactive hydroxyl or keto groups. Gasoline, hexane, benzene and cyclohexane can be mentioned as examples.

The reaction of this invention may be effected with such a small quantity of metal alcoholate that the reducing action produced by the alcoholate is negligible. Primary and secondary alcoholates can be employed but the tertiary alcoholates are more advantageous. In some cases, particularly when primary or secondary alco-

holates are used, I advantageously remove the low molecular alcohol by evaporation, for example in vacuo, at the beginning of the reaction. During the reaction a certain quantity of diol and dione derivatives is formed and it is possible, if desired, to adapt my reaction to the production of these particular compounds. The hydroxy-ketone fraction can be easily separated from the diol-dione fraction by known methods. Either of these fractions can be treated again with a metal alcoholate, preferably a tertiary alcoholate, in accordance with my invention in order to produce an increased yield of the other fraction. Before effecting this re-treatment, one of the components of the fraction to be re-treated may be separated. For example, it is possible to separate testosterone from the hydroxy-ketone fraction by known methods, before re-treatment of the residue. When re-treating the diol-dione fraction, it is advantageous to have present substantially equal numbers of hydroxyl and keto groups.

Which of the two fractions should be re-treated depends, of course, upon whether it is desired to recover one of the hydroxy-ketone compounds, which are formed in the process, or crystallized diols and diones. In the treatment of dehydroandrosterone by my process, for example, it is possible to recover either testosterone or androstendiol and androstendione, the latter compounds being recovered from the diol-dione fraction and the former from the hydroxy-ketone fraction. If it is desired to obtain a hydroxy-ketone compound, the diol-dione fraction may be subjected to a treatment, this fraction usually being mixed with the unconverted hydroxy-ketone which is first separated from the hydroxy-ketone fraction. On the other hand if it is desired to recover diol and dione compounds, the hydroxy-ketone fraction should be subjected to re-treatment. Since substantially no by-products are formed in my reaction, it is possible by successive re-treatments to increase the yield of the desired compound or compounds to approximately the theoretical yield. It is also possible, of course, to obtain by my method various mixtures of compounds having a certain physiological action, for example a greater or smaller action on the growth of the capon's comb with a correspondingly smaller or greater action on the seminal vesicle, this result being possible by controlling the conditions under which the reaction is effected, such as temperature, concentration of solvent and time of reaction, or by choice of the fractions to be re-treated or by mixing the fractions to be re-treated in various proportions.

My invention can be described in somewhat greater detail by reference to the following specific examples which represent illustrative embodiments thereof.

Example 1

I refluxed 20 g. of dehydroandrosterone with 25 g. of tertiary aluminum butylate in 500 cc. of anhydrous benzene for a period of 14 hours. The resulting yellowish solution was shaken with dilute sulfuric acid for a short time to remove the aluminum. The benzene solution was then washed with water, dried with sodium sulfate and subjected to evaporation. A nearly colorless syrup, fraction I, was obtained which was found to have an activity in the capon's comb test which was 2 to 3 times that of the starting material. This syrup was then rubbed with 250 cc. of ether and the resulting mixture was al-

lowed to stand for three days during which it was found that crystals (II) separated, which were found to consist of substantially pure delta-5,6-androstendiol. These crystals were filtered off and, after the ethereal solution was evaporated, a syrup (III) remained. This syrup was then treated with a ketone reagent in order to separate the diols (IV). As ketone reagents it is possible to use semicarbazide, hydroxylamine, beta-inehydrazine-hydrochloride etc. The ketone condensation products were then split up and the syrup (V) thus formed contained the hydroxy-ketones and the androstendione. This syrup was separated by methods known per se into a hydroxy-ketone fraction (VI) and into androstendione by treatment with phthalic anhydride. Chloro-sulfonic acid in pyridine can also be used in this separation.

The hydroxy-ketone fraction (VI) was then treated with a 1 per cent alcoholic digitonine solution, forming a digitonide precipitate which was filtered off and split up by boiling in xylene to obtain a syrupy fraction (VII), which was found to consist mainly of dehydroandrosterone. The filtrate from the digitonine precipitation (VIII) was allowed to stand until crystals separated, these consisting mainly of testosterone. These crystals can be recovered and purified by recrystallization with a yield of 1.5 to 2.2 grams.

If desired, the process described above can be interrupted at any of the intermediate stages indicated. For example, the fractions (I), (III), (V), (VI) and (VIII) are useful for pharmaceutical purposes without further purification. If it should be desired to obtain fraction (VI) in a large yield, the fractions (II) and (IV) and the androstendione from (V) may be united and again subjected to the reaction or added to a subsequent charge of dehydroandrosterone used in a repetition of the process. If it is desired to obtain crystallized testosterone in high yield, this can be accomplished by uniting all fractions obtained prior to the separation of fraction (VIII), as well as the mother liquor from (VIII), this mixture being subjected to a new isomerization treatment or being added to a subsequent charge in a repetition of the process.

Example 2

In this example 10 grams of an extract from urine was used, which was prepared according to the method described by Funk and Harrow (Proc. Amer. Soc. Biol. Chem., 7, LXX, 1931) and which had an activity of 1 international capon's comb unit per mg. This extract was refluxed with 250 g. of tertiary aluminum amyolate in 1.5 liters of anhydrous toluene. After the reaction was completed, the aluminum was removed by shaking with dilute sulfuric acid and the toluene solution was washed with water. The resulting solution may be used as such for pharmaceutical purposes. It was found to show an activity about 3 to 5 times that of the starting material in the capon's comb test. Moreover, in contrast to the starting material, it was found to have a strong action on the primary sexual organs. Thus, in the seminal vesicle test on rats, it was found that 0.3 mg. corresponded to 1 unit. The yield in this reaction was 100 per cent, since the material had not changed in weight during the treatment. Urine extracts obtained by the method described by Butenandt and Tscherning (Z. Physiol. Chem. 167, 229, 1934) can be substituted for that used in the above described reaction.

Example 3

I refluxed a mixture of 24 g. of delta 5-pregnenol-3-one-20 with 600 cc. of toluene and 60 g. of tertiary aluminum butylate for a period of 24 hours. The resulting yellow reaction products were thoroughly shaken with dilute sulfuric acid and then washed with water, the toluene being then removed by evaporation in vacuum. The residue was heated with a mixture of 180 cc. of pyridine and 50 g. of phthalic anhydride on the steam bath for a period of 3 hours, then poured into 2 liters of N/2 NaOH. The reaction mixture was then extracted with ether. The ether solution was thoroughly washed with water, dried with sodium sulfate and the ether was removed by evaporation. Crude progesterone remained behind, which was crystallized from methanol. A yield of 4.3 g. was obtained, having a melting point of 129–130° C.

The aqueous layer obtained as described above was refluxed in the absence of oxygen for a period of 4 hours. After the liquid was cooled, it was extracted with ether. The ether solution was washed with water and the ether removed by evaporation. During this evaporation crystals separated out consisting of delta 5-pregnanediol-3,20. The remaining solution, containing approximately 150 cc. of ether was allowed to stand for 24 hours. The crystals formed in the solution were filtered off and the mother liquor was concentrated by evaporation. The residue obtained was heated in 150 cc. of glacial acetic acid with 25 g. of Girard-reagent-T on the steam bath for 20 minutes. The solution was then separated by adding ether and an aqueous alkaline solution into an etheric ketone-free fraction and an aqueous ketonic fraction (see Girard, Sandulesco, *Helv. Chim. Acta* 19, 1095, 1936). The ketone-free fraction consisted for the main part of delta 5-pregnanediol-3,20. The total yield of this substance together with the crystals already recovered amounted to 4.8 g. The aqueous fraction was found to contain the hydroxy-ketones in which unchanged delta 5-pregnenol-3-one-20 was present. The latter was separated by precipitation with digitonine in 90 per cent alcohol. The clear solution was diluted with water, extracted with ether and the etheric layer was subjected to evaporation. The residue was subjected to sublimation in high vacuo (140° C. and

0.01 mm. mercury pressure). Upon the addition of acetone it was found that crystals separated after a short time, which crystals were found to melt at 161–162° C. These crystals were found to be identical to the delta 4-pregnenol-20-one-3 obtained by Butenandt and Schmidt (*Ber.* 67, 1901, 1934) by means of a different process.

If it is desired to prepare progesterone, the whole hydroxy-ketone fraction can be added to the following charge of starting material, preferably after a preliminary distillation in a high vacuum.

Example 4

I refluxed 500 mg of delta 5-pregnene-diol-3,21-one-20 with 500 mg. of tertiary aluminum butylate and 20 cc. of benzene for several hours in an oil bath. Ether was then added and dilute sulfuric acid was added to remove the aluminum. The etheric solution was washed with water, dried and then evaporated.

By treatment with digitonine in alcohol of about 80 per cent concentration, approximately half the material was found to be precipitated as the digitonide. The compound precipitated by the digitonine was regenerated but was found to be inactive. The unprecipitated fraction was freed from the excess digitonine and then acetylated at room temperature by treatment with acetic acid anhydride in pyridine. The reaction products were poured into water and dissolved in ether, the pyridine being removed by repeated washing of the etheric solution. The solution was then dried and subjected to evaporation. It was found that 1–2 mg. of the residue, when dissolved in oil, gave a strong cortine activity in the Everse-de-Fremery test while the starting material was substantially inactive in this test. The active component in this product is believed to be the 21-acetate of delta 4-pregnene-dione-3,20-ol-21.

In the above reaction it is evident that theoretically no less than 8 different compounds are formed.

While I have described what I consider to be the most advantageous embodiments of my process, it is evident that the specific procedures disclosed can be varied widely without departing from the purview of this invention.

RUPERT OPPENAUER.

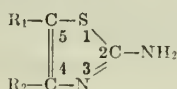
ALIEN PROPERTY CUSTODIAN

PROCESS FOR PREPARING AMINOTHIAZOL-DERIVATIVES

Zoltán Földi, Rezső König, and István Demjén,
Budapest, Hungary; vested in the Alien Prop-
erty Custodian

No Drawing. Application filed May 13, 1940

The present invention relates to new industrial products, to diarylsulfonyl-derivatives of 2-aminothiazols of the formula:

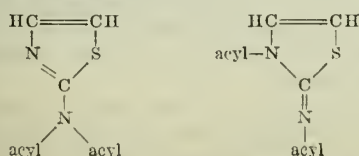


one of the arylsulfonyl groups being bound to the amino-group in position 2, the other being bound to the nuclear N-atom of the thiazol-nucleus. R_1 and R_2 means in the above-standing formula members of the group consisting of: H, alkyl, oxoalkyl, carboxyl, carbalkoxyl. Preferred representatives of the new products are those in which R_1 means H-atom and R_2 means either H or an aliphatic radical, such as methyl, ethyl. Especially valuable diarylsulfonyl products are those in which the arylsulfonyl groups are benzolsulfonyl groups, the benzene-ring being substituted in the para-position by a member of the group consisting of H, acyl, NH , NO_2 . In these compounds the position 4 of the thiazol-nucleus preferably contains a member of the group consisting of H, alkyl-radical. The present invention relates further to diaryl-sulfonyl-derivatives of 2-aminothiazoles in which one of the arylsulfonyl groups is bound to the amino-group in position 2, while the other is bound to the nuclear N-atom of the thiazole-nucleus, at least one of the arylsulfonyl groups being a p-acylamino-benzolsulfonyl group.

A further object of the present invention is to provide for processes to prepare the new diarylsulfonyl-derivatives. The process consists in subjecting 2-aminothiazols to the action of acylating agents, generally used to introduce arylsulfonyl groups and in isolating from the reaction mixture the acylation products containing two arylsulfonyl groups. One may use as acylating agents those ones which are generally used to introduce amino-arylsulfonyl groups. Such acylating agents are e. g. the p-acylamino-benzol-sulfonyl-halogenides.

The introduction of two arylsulfonyl groups can be also carried out in two separate steps, in each step only one arylsulfonyl group being introduced.

Amino-thiazole, such as the 2-amino-thiazol, are supposed to show two tautomeric forms. Therefore, two possibilities exist for the structure of diacyl-amino-thiazol derivatives as illustrated on the following formulae:



In these formulae the "acyl" means any aryl-

sulfonyl group such as an acylamino-benzolsulfonyl group. Considerable difference exists between the fixation of the two arylsulfonyl groups, as one of these groups can be easily split off from the molecule by hydrolysis, resulting mono-arylsulfonyl derivative which contains the remaining arylsulfonyl group bound to the amino group in the position-2. Our further investigations proved that the diacyl products obtained according to the present invention correspond in their structure to the right-hand formula. This fact could be established by introducing two different acyl groups in two separate steps resulting thus two different diacyl derivatives depending on the sequence of the two acylations.

The acylation according to present invention can be effected in various manners. The acylating agent is preferably used in a proper excess, the more as the theory requests at least two moles of the acylating agent. The acylation is preferably carried out in the presence of a diluent such as acetone, using preferably an agent to bind the acid resulting in the acylation. One may use, as such an agent, an alkali bicarbonate, such as sodium bicarbonate. One may use for the same purpose other ingredients, as well, such as tertiary bases, for instance dimethylaniline. By using dimethylaniline the main products of the acylation is the di-(acetamino-aryl-sulfonyl)-derivative even in cases when only one mole of the acylating agent, such as of p-acetyl-amino-benzol-sulfonyl-chloride, has been used.

One may further use as agent to bind acid aqueous alkalis, as well, such as 2-normal sodium hydroxide solution; in this case the acylation is preferably carried out in acetone as medium at temperatures not exceeding 50°.

After terminating the acylation, the reaction mixture can contain—although unconsiderable amounts—monoacyl derivatives, which can be eliminated from the diacyl derivative by means of extraction by aqueous alkalis. The monoacyl derivatives are, namely, soluble in alkalis.

As acylating agents sulfonyl-halogenides can be preferably used, such as p-acetamino-benzol-sulfonyl chloride, p-nitro-benzolsulfonyl chloride, benzolsulfonyl chloride, etc.

The amino-thiazols, as the 2-amino-thiazol, can contain substituents in the heterocyclic ring, such as alkyl groups (2-amino-4-methyl-thiazol) or aryl groups (2-amino-4-phenyl-5-methyl-thiazol).

The di-(arylsulfonyl)-amino-thiazols separated from the reaction mixture can be subjected to a further treatment, namely to a hydrolysis, one of the arylsulfonyl groups being split off completely from the molecule, the acyl group being split likewise from the remaining arylsulfonyl group, if the latter contained an acylamino group.

The hydrolysis can be carried out directly with the reaction mixture, as well. The hydrolysis can be effected by diluted alkali solutions, such as sodium hydroxide of 8-10% or by diluted acids, such as by diluted hydrochloric acid.

The di-(arylsulfo)-amino-thiazols are sensible to alcohols. By boiling a di-arylsulfonyl derivative in an alcohol, preferably in absolute ethyl-alcohol, containing a haloid acid, preferably dry hydrochloric acid, the arylsulfonyl group bound to the tertiary nitrogen atom of the heterocyclic ring is split off completely and if the arylsulfonyl group contained an acetyl amino group as substituent, the acetyl groups are likewise split off, in the form of acetic ether.

The diacyl products of the present process can also be obtained by effecting the acylation in two steps. In the first step one acetyl group is introduced into the amino group in position 2, this first acylation being preferably carried out by the method described already in our U. S. A. Application No. 267,168. The monoacyl derivative, thus obtained is now acylated in a further step. The acylation in this second step is preferably carried out by means of acylation methods as described above for the preparation of the diacyl derivatives in a single step. The introduction of the two acyl groups in two steps give possibility to introduce different acyl groups into the molecule which is not at all possible by effecting the acylation in a single step. Different acyl groups can preferably be the following: p-acylamino-benzolsulfonyl, p-nitro-benzolsulfonyl, p-acylaminobenzolsulfonyl, p-acylamino-o-alkoxy-benzolsulfonyl, p - acetamino - m-alkyl-benzol-sulfonyl, benzol-sulfonyl-, etc. groups.

Some of the products of the process are starting materials in the preparation of anticoccic products, others being themselves of anticoccic action, for instance of antipneumococcic or antigonococcic action.

Further details are to be found in the following examples:

Examples

1. 10 grams (0.1 g mol) of 2-amino-thiazol, 50 grams (0.215 g mols) of p-acetamino-benzol-sulfonyl-chloride, 20 grams of sodium bicarbonate and 100 ccs of dry acetone are stirred for about 2 hours in the water bath. The acetone is then evaporated and 200 ccs of water added. The di(p-acetamino-benzolsulfo)-2-amino-thiazol remains undissolved and isolated by suction, washed and dried in vacuo. Its amount is nearly the theoretical. The produce can be purified by extracting it (after pulverisation) with diluted sodium hydroxide solution and washing with water. In this experiment mono-acyl derivatives do not result however, in practical amount.

The raw product can be recrystallised for instance as follows:

10 grams are dissolved in 100 ccs of boiling acetone of 80%. On cooling the product crystallises in uniform needles containing solvent of crystallisation. The melting point is rather unsharp, the product becomes at about 200° brownish and decomposes at 260°. The melting point does not become sharp on further recrystallisation from acetone. The product repeatedly crystallised from acetone shows on analysis a relation of 1 atom of sulfur to 1.31 atoms of nitrogen, i. e. a relation of 1 atom of sulfur to 4 atoms of nitrogen. The product persistently retains the solvent of crystallisation which can be eliminated

therefore only by drying at higher temperature, however incompletely.

On hydrolysis by alkali one of the acyl-amino-aryl-sulfo-groups is split off as shown in the following:

10 grams of the raw di-(p-acetyl-amino-benzolsulfo)-2-amino-thiazol are boiled in 100 ccs of sodium hydroxide of 10% for about an hour. The excess of the alkali is now neutralized by hydrochloric acid at the end by acetic acid using lithmus as indicator. The p-amino-benzolsulfo-2-amino-thiazol separates in nearly theoretical amount. It melts at about 203°. If further purification is wanted, it may be dissolved in the threefold amount of hot sodium hydroxide of 20%. On cooling the sodium salt separates. It is suctioned, washed by sodium hydroxide of 20%, then dissolved in hot water and—after treating with animal charcoal—the filtrate is acidified first with hydrochloric acid, at the end by acetic acid. The product shows antipneumococcic action.

2. 10 grams (0.1 g mol) of 2-amino-thiazol, 25 grams (0.107 g mols) of p-acetamino-benzolsulfonyl chloride are dissolved in 100 ccs of acetone. While stirring, 57 ccs of 2-normal sodium-hydroxide are dropped at 36°. The reaction mixture becomes practically neutral to lithmus. After a short time the reaction mixture solidifies in crystals. On further standing the crystals are suctioned, washed by aqueous acetone and by water and dried in vacuo. One obtains about 15 grams of di-(p-acetyl-amino-benzolsulfo)-2-amino-thiazol. The product melts unsharply between 130-150°. By extracting with tenfold amount of cold normal sodium hydroxide small amounts of contaminations can be eliminated. A recrystallisation from acetone of 70% can be used for further purification. The product contains solvent of crystallisation. On analysis it shows 18.4% of sulfur and 10.7% of nitrogen. The atomic relation of sulfur and nitrogen is thus S:N=3:4. These crystals on recrystallisation from alcohol show the following behaviour: 1 g of the product dissolves in 10 ccs of boiling alcohol, followed rapidly by separation of great amounts of crystals which do not dissolve on addition of further amounts of boiling alcohol. After cooling the snowwhite crystal mass is suctioned. At the determination of the melting-point one may observe a sintering at about 215° and a decomposition at about 250°.

This product yields on hydrolysis by means of sodium hydroxide the mono-(amino-benzolsulfo)-amino-thiazol described already in example 1.

3. 10 grams (0.10 g mol) of 2-amino-thiazol, 25 grams (0.10 g mol) of p-acetyl-amino-benzol-sulfonyl chloride, 25 ccs of dry acetone and 12.1 grams (0.10 g mol) of dimethyl-aniline are kept 2 hours on the hot water bath, then the acetone evaporated. On addition of 150 ccs hydrochloric acid of 5% one obtains a blueish-greenish crystalline precipitate which is suctioned, washed by water then by an aqueous sodium bicarbonate solution, by water again and dried. One obtains about 18 grams of the diacyl derivative showing an unsharp melting point between 130 and 160°. It does not dissolve in diluted sodium hydroxide.

On hydrolysing by alkali such as by sodium hydroxide, one obtains the p-amino-benzolsulfo-2-amino-thiazol.

One may proceed as given above, starting from 2-amino-4-methyl-thiazol or from 2-amino-4-phenyl-5-methyl-thiazol, obtaining the corresponding acylated products.

On starting for instance from 2-amino-4-methyl-thiazol one obtains the di-(p-acetyl-amino - benzolsulfo) - 2 - amino-4-methyl-thiazol which yields on hydrolysis by means of sodium hydroxide of 10% the p-amino-benzolsulfo-2-amino-4-methyl-thiazol melting at about 243°.

On acylating p-acetamino-benzolsulfo-2-amino-4-methyl-thiazol by means of p-acetamino-benzolsulfonyl-chloride, one obtains the di-(p-acetamino-benzolsulfo) - 2 - amino-4-methyl-thiazol mentioned above or in a more correct nomenclature: the 2-(p-acet-amino-benzol-sulfinido) - 3-(p-acetamino-benzolsulfo) - 4 - methyl-thiazoline. The melting point of this product varies depending on the solvent used for recrystallisation. Crystallised from alcohol it melts at about 250°.

The same product can be obtained in excellent yield by starting from 11.4 grams of 2-amino-4-methylthiazol by dissolving it in 100 ccs of dry acetone and adding 50 grams of p-acetamino-benzolsulfonyl chloride and 25 grams of finely pulverized sodium bicarbonate. One stirs for about half an hour at about 20° and then for about two and half hours in the water bath of 65°. Now the acetone is distilled off at common pressure and finally in vacuo one adds 200 ccs of water. The remainder is acidified with acetic acid. The precipitate is suctioned and washed by water. The raw product is extracted by an ice-cold 0.5 normal sodium hydroxide and suctioned and thoroughly washed with water. The product after having been boiled with alcohol melts at about 250°.

4. 10 grams of 2-amino-thiazol, 17.6 grams of benzol-sulfonyl chloride, 10 ccs of dry pyridine and 25 ccs of acetone are boiled for 2 hours. Then the acetone is evaporated. On addition of 100 ccs of water to the remainder, the benzol-sulfo-2-amino-thiazol crystallizes. It can be purified by converting it into the sodium salt and regenerating it from this salt. It melts at about 175°.

2.2 grams of the above described benzolsulfo-2-amino-thiazol and 7.5 grams of p-acetamino-benzolsulfonyl chloride and 32 ccs of 2-normal sodium hydroxide are added in portions to the reaction mixture kept at 15°. The materials dissolve at the beginning and after addition of the total amount of the alkali an oily precipitate occurs which soon crystallizes. One obtains 11 grams of 2-(benzolsulfinido) - 3 (p-acetamino-benzolsulfo) - thiazoline, that is the diacyl derivative of the tautomeric form of 2-amino-thiazol. It melts at about 120°.

5. 3 grams of p-acetamino-benzolsulfo-2-amino-thiazol (obtained as described in our U. S. A. application No. 267,168), 1.8 grams of benzolsulfonyl chloride, 15 ccs of acetone and 10 ccs of 2-normal sodium hydroxide are worked up as given in the preceding example. The raw product thus obtained is extracted by diluted sodium hydroxide. One obtains the 2-(p-acetamino-benzolsulfinido) - sodium - hydroxide. One obtains the 2-(p-acetamino-benzolsulfinido) - 3-(benzolsulfo) - thiazoline, that is as well a mixed diacyl derivative contains the arylsulfo groups in an exchanged position relating to the product described in the preceding example. The product of the present example melts at about 180°.

6. 3 grams of p-acetamino-benzolsulfo-2-amino-thiazol and 2.5 grams of p-acetamino-benzolsulfonyl chloride are mixed with 20 ccs of acetone and 10 ccs of normal sodium hydroxide are dropped at 25-30°, while shaking. The alkaline reaction disappears soon, the acyl product dissolves and on short standing crystallisation occurs. The crystals are collected, extracted by 50 ccs of normal sodium hydroxide, suctioned and washed by water and dried in vacuo. The dry di-(p-acetamino - benzolsulfo) - 2 - amino-thiazol shows an unsharp melting point; it melts completely at about 180°.

One may proceed similarly on starting from corresponding derivatives of 2-amino-thiazols substituted in the heterocyclic ring, for instance starting from the corresponding derivative of 2-amino-4-methyl-thiazol.

7. The alcoholysis is shown in the following example: 10 grams of di-(p-acetamino-benzolsulfo)-2-amino-thiazol are refluxed for about half an hour with 50 ccs of abs. alcohol, containing at about 4% of dry hydrochloric acid. One may observe the formation of acetic ether. After cooling, the crystals are suctioned and washed by alcohol. One obtains the p-amino-benzolsulfo-2-amino-thiazol which is partly present in form of its chlorhydrate. This product is stirred with a watery solution of sodium acetate yielding p-amino-benzolsulfo-2-amino-thiazol now free from its salt formed by hydrochloric acid. One may proceed in similar manner starting from the diarylsulfo derivatives of 2-amino-4-methyl-thiazol.

8. 1.14 grams of 2-amino-4-methyl-thiazol are dissolved in 5 ccs of dry acetone, 2.5 grams of sodium bicarbonate and then 2.24 grams of p-nitro-benzolsulfonyl chloride added. After heating a further portion of 2.25 grams of p-nitro-benzolsulfonyl chloride is added. The reaction mixture is boiled for about ¾ hour and then the acetone evaporated off. On addition of water to the residue, one obtains a yellow solid precipitate which is suctioned, washed with water and dried in vacuum exsiccator. This product of about 4 grams is stirred for a few minutes by 25 ccs of 0.5-normal sodium hydroxide, then suctioned, washed by water and dried in exsiccator. It melts at about 196°. This product is the di-(p-nitro-benzolsulfo) - 2-amino-4-methyl-thiazol. It can be recrystallised from the fortyfold amount of boiling anizol. The melting-point rises thus to 214°.

From the alkaline mother liquors one obtains on acidification by hydrochloric acid the mononitro-benzolsulfo-derivative which melts in this state at about 196°. On dissolving it in sevenfold boiling acetone and adding fifteenfold amount of water, this product crystallises in well developed uniform yellow plates and shows a melting point of about 200°. This product yields on catalytic hydrogenation (palladium as catalyst) in an alcoholic suspension the p-amino-benzolsulfo-2-amino-4-methyl-thiazol melting at about 240°.

ZOLTÁN FÖLDI.
REZSŐ KÖNIG.
ISTVÁN DEMJÉN.

ALIEN PROPERTY CUSTODIAN

METHOD OF MANUFACTURING PRODUCTS FROM RUBBER AND PRODUCTS OBTAINED THROUGH SAID METHOD

André Chomette, Neuilly-sur-Seine, and Robert Thiollet, Paris, France; vested in the Alien Property Custodian

No Drawing. Application filed May 15, 1940

The rubber industry makes use, at the present time, of certain organic products in order to accelerate vulcanization or in order to improve the preservation of vulcanized rubber articles.

These products, which belong to various chemical species, comprise, in particular, compounds in the composition of which amine groups are present. Such products quickly assume intensive greyish or brownish colorations when they are exposed to the combined actions of air and light.

As they are soluble in rubber, these products have a tendency to diffuse in the vulcanized mixtures, while forming on their surface a highly coloured layer. This coloration is not visible in the case of mixtures of black or dark colour, but it makes it wholly impossible to make use of certain accelerators and anti-oxygen bodies in the case of while or light coloured rubber mixtures.

It is easy to select non-colouring accelerators. Thiurames, thiazoles and dithiocarbamates do not produce any modification of the shade of the objects subjected to the sun light.

On the contrary, the most efficient antioxygen bodies, such as phenyl-naphtylamines or aldol-naphtylamines, produce an intensive brown coloration, when they are subjected to the same conditions.

It has already been endeavoured to reduce this drawback by preparing anti-oxygen bodies which are little soluble in rubber and more stable against the action of light. These products diffuse but very slowly toward the surface and, accordingly, their coloration is much less intensive. For instance, it has already been suggested to make use of phenol function products, which are less soluble in rubber than amine derivatives, and assume a lesser coloration under the action of light, for instance parahydroxyphenyl, beta-naphtol, methylene di-beta-naphtol, and so on.

However, even when making use of anti-oxygen bodies of this kind, the coloration of the objects subjected to the action of light is still considerable. Ultra-violet rays considerably increase the formation of this coloration.

If, on the surface of a vulcanized mixture containing an anti-oxygen, there is applied a film of a transparent substance capable of stopping ultra-violet rays, it is found that the brown colouring takes place much more slowly at the places where the film is applied.

However, it would be little efficacious to protect the rubber objects by coating them with a film opaque to ultra-violet rays. This film would most probably be quickly eliminated, especially when the problem is to protect cushions or mats intended to undergo friction of other objects or mechanical stresses.

The object of the present invention is to pro-

vide a method of producing rubber articles which avoids the above drawbacks.

According to the essential feature of the present invention, we incorporate, into mixtures consisting chiefly of rubber, substances capable of stopping ultra-violet rays. These substances constitute a screen which is opaque to the rays in question and which, therefore, opposes the development of the colouring due to the presence, in rubber, of some auxiliary products.

We have obtained a great number of mixtures of the kind above referred to by incorporating therinto various substances which are opaque to ultra-violet rays, and we have determined the proportions of said substances to be utilized in order to obtain a satisfactory protection against the action of light.

We have found that the substances with which the most satisfactory results are obtained are the following: urea, thio-urea, their products of condensation with aldehydes, their substitution derivatives and their salts, such for instance as urea benzoate, or the like.

Other substances which permit of obtaining a satisfactory result are artificial plastic matters, such as glycerophthalic resins, and formophenol resins which do not themselves produce a coloration of rubber, such substances producing a good protection.

It suffices to employ from 0.5 to 10 per cent of these matters, with reference to the weight of the mixture, for obtaining a highly satisfactory protection.

In order to facilitate the dispersion of the protective matters, it may be advantageous to incorporate them into the rubber mass at the same time as a dispersing body or after having dissolved them in a suitable solvent.

We also consider the formation of artificial resins "in situ." In this way we obtain an intimate mixing of the plastic matter and of the rubber mass of the article.

Example 1

The following mixtures are prepared for comparison purposes:

	A	B
Crepe	100	100
Zinc oxide	100	100
Sulphur	2	2
Zinc ethylphenyldithiocarbamate	1	1
Phenyl-beta-naphtylamine	1	1
Glycero-phthalic resin	0	5

The vulcanized mixtures are exposed to the action of sun light.

After three days of action, mixture A has assumed a high coloured brown shade, while mixture B is of light shade.

Example 2

The following mixtures are prepared for comparison purposes:

	A	B
Crepe.....	100	100
Zinc oxide.....	100	100
Sulphur.....	2	2
Zinc ethylphenyldithiocarbamate.....	1	1
Methylene-di-betanaphtol.....	1	1
Aqueous solution of dimethylolurea of 50 per cent.....	0	8

In the course of the vulcanization operation dimethylolurea condenses into a plastic matter 15

which is perfectly well dispersed in the whole mass of the mixture.

After several days of exposition of the products to the action, the sample obtained with mixture B is not coloured, while the same obtained with mixture A has become a pinkish grey. 5

The method according to the invention which permits of avoiding coloration of objects under the influence of light applies to the protection of the objects manufactured from coagulated rubber or latex, from artificial elastic matters similar to rubber, or from their aqueous dispersions. 10

ANDRÉ CHOMETTE.
ROBERT THIOLLET.

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF CARPETS, LININGS
OR THE LIKE

Jean Mercier, Neuilly-sur-Seine, France; vested
in the Alien Property Custodian

Application filed May 15, 1949

The present invention relates to the manufacture of carpets, linings, or the like, consisting chiefly of rubber or the like, said linings being in particularly intended for making non-slipping surfaces, for instance for the running boards of motor vehicles, and, especially for certain portions of airplane wings.

As a matter of fact, in the last mentioned case, it is important that mechanics should be able to circulate, during flight, on the wings of an airplane, under the best possible conditions of safety, for instance for supervising the running of the engines or for performing any repairs as may become necessary immediately.

The object of the present invention is to provide a non-slipping lining of the type above described, which complies with the conditions above stated and which can be manufactured very easily and at a low cost.

According to the essential feature of the invention, I vulcanize a mixture including a rubber combination, of any type, either conventional or not, mixed with a certain amount of cereal straw, the latter being optionally divided into elements of relatively small size.

I have found that surfaces made of such a composition, in the form of linings, carpets, or the like, have non-slipping properties which are remarkable, especially when they are sprayed with or immersed in oil.

Other features of the present invention will result from the following detailed description of some specific embodiments thereof.

A preferred embodiment of the present invention will be hereinafter described, with reference to the accompanying drawing, given merely by way of example, and in which:

The only figure is a sectional view of a lining made of a composition according to the invention, as fixed on a portion of the upper face of an airplane wing.

As shown by this drawing, the rubber mass 1 contains, embedded therein, particles or elements of straw 2, which give the surface of the lining the desired non-slipping properties.

In order to obtain such a composition of matter, I proceed in the following manner:

I prepare the rubber composition in the form of coagulated resin, latex, or the like. The straw, which may have been preliminary treated or not in order to give it any desired supplementary property, is cut into elements of suitable length, said 1 centimeter. It should be well understood that straw can be employed, according to the invention, without so dividing it into elements, in its natural state. The straw is incorporated into the rubber composition. Then the whole is vulcanized according to the needs.

I will now describe an example of application of the method according to the invention:

The rubber liquid above referred to is of the following composition:

	Parts in weight
Gum -----	100
Zinc -----	10
Stearic acid -----	1
Litopone -----	25
Anti-oxidizing, accelerator, Sulphur-----	5

To this mixture, I add 75 parts in weight of cereal straw, divided into elements of approximately 1 centimeter.

The mixture is vulcanized for 30 minutes approximately, at a temperature of about 135° C.

Of course, the example above set forth has no limitative character.

The rubber that is employed may be either natural rubber or synthetic rubber, of any suitable type.

As above stated, the straw that is incorporated into the rubber composition may be either cut into elements or employed in its natural state, the stirring of the mixture of straw and rubber being pursued until the desired dispersion of the whole is obtained.

It is important to note that cereal straw is, as a rule, impervious to water, and, accordingly, it can be employed, in the mixture above set forth without subjecting it to any preliminary water-proofing treatment. This is a great difference with what happens, for instance in the case of wood. As a matter of fact, wood, in order to be employed in admixture to a rubber composition, must necessarily be crushed or cut into small shavings, or reduced to the state of saw dust. But the shavings or saw dust thus obtained are highly hygroscopic, and therefore necessitate a supplementary drying treatment before being introduced into the rubber composition. Such a treatment is avoided with the method according to the present invention, which makes use of straw.

Of course, the straw to be incorporated into the mixture can be subjected to any desired treatment, as above mentioned, for instance for making it fire-proof or protecting it against the attack of fat and oil. Such a treatment can be, for instance, effected, by means of borax, ammonium nitrate, and similar products.

Of course, the invention covers the mats, carpets, linings obtained from matter made according to the method above set forth.

In a general manner, while I have, in the above description, disclosed what I deem to be practical and efficient embodiments of the present invention, it should be well understood that I do not wish to be limited thereto as there might be changes made in the accessory steps of the method without departing from the principle of the present invention as comprehended within the scope of the appended claims.

JEAN MERCIER.

March 26, 1891

Dear Sir,

I have the honor to acknowledge the receipt of your letter of the 24th inst. in relation to the matter of the purchase of the land for the proposed canal.

I am sorry to hear that you are not satisfied with the price offered for the land. I have endeavored to secure the best price possible for the land, but I am sure you will understand that I have done my best.

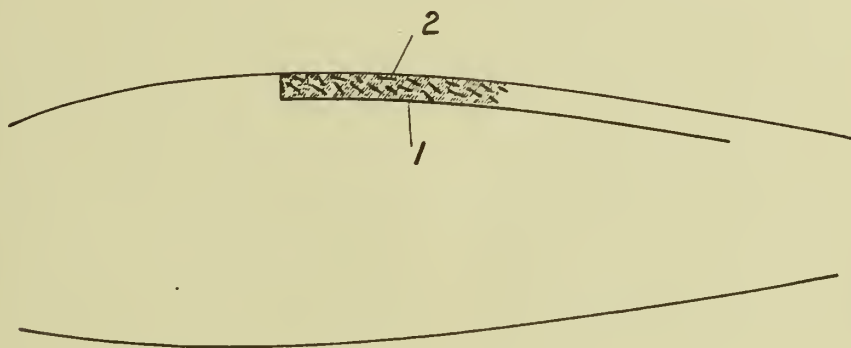
I am sure that you will be satisfied with the price offered for the land, and I am sure that you will be satisfied with the price offered for the land.

I am, Sir, very respectfully,
Your obedient servant,
J. H. [Name]

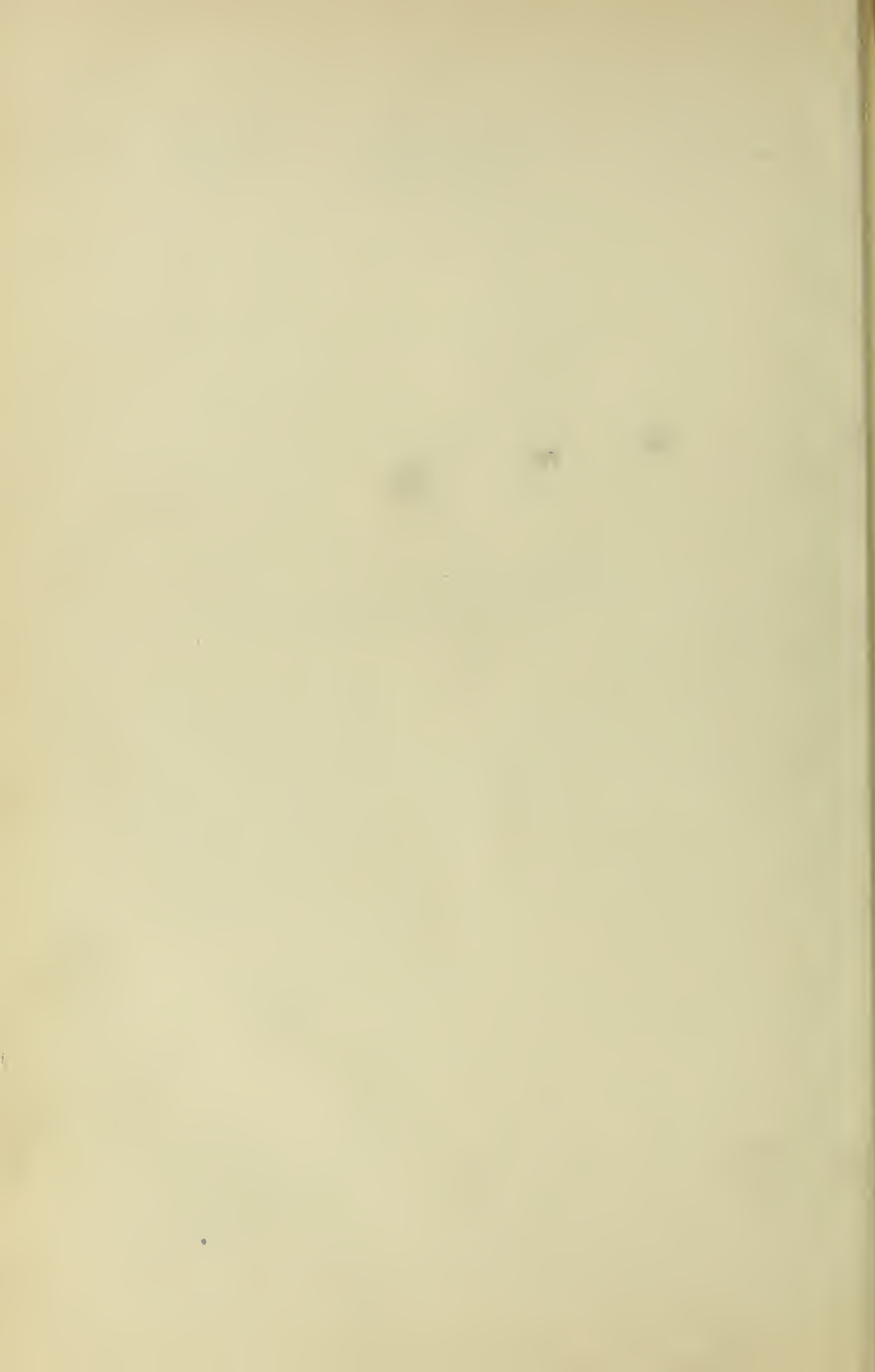
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Jean Mercier
INVENTOR
By *[Signature]*
his ATTY.



ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF CYCLIC AMIDINES AND ARTIFICIAL MATERIALS PRODUCED THEREOF

Paul Schlack, Berlin-Treptow, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed May 18, 1940

This invention relates to the manufacture of cyclic amidines and artificial materials produced thereof.

It is an object of the present invention to produce reactive polyfunctional amidine compounds.

A further object is the production of polyfunctional amidine compounds which may be transformed directly into synthetic materials.

These and other objects will be apparent from the following description.

It has been found, that polyfunctional amidine compounds of wide use, which are suitable for the synthesis of artificial materials and which may be worked up under certain conditions directly into such artificial material, are obtained, if O-substituted enol compounds of lactams are caused to react with polyfunctional compounds containing more than one amino group or at least one amino group and at least one hydroxyl or sulfhydryl group of aliphatic character or at least one carboxyl group or a transformed carboxyl group e. g. a nitrile group, ester group or amide group, whereby, if necessary, either the lactam derivatives or the counter components containing amino groups may be present in the form of salts. If a polyvalent amino compound functioning as counter component is saturated with a polyvalent carboxylic acid, primary reaction products are obtained, which, if further heated at a correspondingly high temperature of for instance 170–270°C, turn into high molecular polyamides.

The primary reactions with the lactam derivatives were found to run off as a rule very smoothly, though side reactions on account of ring cleavage have to be taken into consideration at least with lactams having more than six ring members. For this process there may be employed in principle oxygen derivatives, for instance O-alkyl ether or O-ester of all lactams. For the synthesis of polyamide artificial materials, however, especially those products are valuable which are derived from lactams with at least seven atoms in the ring. As starting material there may be mentioned the following: the O-methylethers from γ -butyrolactam, the O-methylethers from δ -valerolactam, the O-methylethers from ϵ -caprolactam, the O-methylethers of the C-methyl- ϵ -caprolactams and the O-methylethers of the lactam of the β -amino heptylic acid (superone isoxime), further the O-n-butylether and the O-phenylether and the benzenesulfoester of the enolic ϵ -caprolactam.

The O-alkylethers are obtained in the usual manner by the reaction of the lactimsulfoester

with alcohols or alcoholates, furthermore, as it was found, by the reaction of the lactams with dialkylsulfates or arylsulfo acid esters, preferably in the presence of indifferent solvents like benzene or xylene. Also the alkylsulfonic acid esters, as further was found, are reactive and may be used for the reactions either as such or transformed into the distillable lactim ethers. The alkylsulfonic acid esters are obtainable, if alkyl sulfo chlorides, for instance propane sulfo chloride or propane disulfo chloride are caused to react with lactams in the presence of tertiary amines, for instance pyridine.

For the transformation of the lactam derivatives (lactim compounds) into amidines for instance the following polyfunctional amino compounds or, if the free lactimether are used also their salts, for instance with hydrochloric acid, toluene sulfo acid, adipic acid, sebacic acid may be employed: Ethylenediamine, diethylenetriamine, polyethyleneimine, putrescin, hexamethylenediamine, symm. dimethylhexamethylenediamine, octamethylenediamine, $\beta\beta'$ -diaminodiethylether.

Other suitable amino compounds are: 3,3'-diamino-dipropylsulfide, 3-aminopropandiol-1, 5-aminopentanol-1, 5-aminoamylmercaptan-1, 6-aminoheptane acid, (sodiumsalt), 6-amino-hexane acid nitrile, 6-aminoheptane acid methylester.

The change into amidine compounds may be accomplished already by using the primary reaction products produced for instance by the unification of lactam and dimethylsulfate, if the formation of the lactim compounds is brought about sufficient smoothly. This simplifies the procedure very much. Usually the reaction is carried out in aqueous, alcoholic or alcoholic-aqueous solution. In some cases, especially with very unstable cyclic compounds, the use of water, and hydroxyl-free solvents is preferred, e. g. tetrahydrofuran, dioxane, glycol formale, methylenechloride, benzene. Needless to say also the solubility of the reaction mixture and the capability of being isolated is important for the selection of the solvent. By the reaction of the free lactim ethers with amines, if necessary in the presence of a small portion of catalytically effective hydrogen halide, the amidines are obtained immediately in the form of the free bases. If one starts from lactim ether salts, the corresponding amidine salts are obtained. The same applies to the possible reaction of free lactim ethers with amine salts and the reaction of amine bases with sulfoesters of the enolic lactams. When working with delicate salts it is of advantage to use wa-

ter- and hydroxyl-free solvents so that ring cleavage is avoided. Hereby is useful, that the addition compounds of diethylsulfates and arylsulfonic acid esters with many lactams were found to be soluble in hydrocarbons containing chlorine in benzene. From these solutions the free ethers may be obtained by discharging them into protassium carbonate solution and purifying them by distillation. Also by a double-reaction with salts of other acids, e. g. of dicarboxylic acids, valuable intermediate products adapted for artificial materials may be precipitated.

The products according to this invention are most useful as such or in the form of their reaction products as auxiliary agents in the textile industry and related branches of the chemical technology. They are especially adapted as intermediate products for the production of synthetic resins or artificial materials. Such products were obtained, if the reaction product of the lactim compounds with at least two amino groups or with amino groups and at least one hydroxyl- and sulfhydryl group are heated up with di- or polycarboxylic acids or, if the products, still containing carboxyl groups besides the newly formed amidine groups, are condensed with themselves in the heat or finally, if products showing still transformed carboxyl groups besides the amidine groups, e. g. nitrile groups and carboxyl acid ester groups are heated up at higher temperatures, for instance 150–300°C, in the presence of water or compounds capable of splitting off water, for instance condensable amino acids or salts of diamines and dicarboxylic acids.

Instead of the free amidine compounds also salts of these compounds with volatile acids like carbonates and especially formates, also products with formylated amino groups may be used. If nitrile compounds are used, one works according to German Patent application I. 63 110 IVd/12 o, filed December 7, 1938; for formyl compounds see German Patent application I. 63 127 IVd/12 o, filed February 7, 1939 (Process for the production of high molecular linear polyamides).

If bifunctional compounds according to this invention are condensed with dicarboxylic acids or derivatives of such acids, if necessary in the presence of water, alcohol or compounds capable of splitting off water, especially also of products forming condensation polymers by dehydration, like ω -amino acids, ω -oxy acids or of mixtures of about equivalent portions of $\omega\omega$ -diamines or $\omega\omega$ -dicarboxylic acids and if necessary of reaction accelerating or regulating modifying agents, for instance mineral acids or compounds splitting off such acids, like hydrochloric acids, toluene sulfo acid, benzylchloride or of salts of bases with strong acids like ammonium chloride, hydrochlorides of amines or amino acids, linear fusible high-polymers are obtained, which may be worked off into filaments, foils or three-dimensional structures, for instance dyecasting compositions, provided the chain is sufficiently long. Modifying agents, for instance hydrogen halides, may be contained in definite portions also already in the intermediate products, for instance if the reaction of the lactim ethers with free diamines or with salts of diamines and dicarboxylic acids is carried out in the presence of small portions of hydrogen chloride, for instance 1/400–1/25 mol for two mol lactam, and if then the condensation is continued without purification, in the first case by adding a nearly equivalent portion of dicarboxylic acid calculated by titration. The condensations may take place at ordi-

nary, increased or reduced pressure. It is often useful to carry out the first step under pressure, whereby the reaction may be considerably accelerated. The increase in pressure may be accomplished by adding indifferent liquids of low steam-pressure, by adding water or alcohol, by alcohol formed during the reaction or by forcing in an indifferent gas, for instance nitrogen.

If products containing more than two functional groups are used, three-dimensional more or less insoluble and unfusible structures are obtained. Such products may be formed in the way of phenoplasts (condensation products of phenols and formaldehyde) or aminoplasts (condensation products of urea and/or thiourea with formaldehyde) by working them off in a low polymeric state and by a subsequent hardening process, if necessary mixed with filling materials. In most cases it is preferable to work off the products with more than two functional groups together with bifunctional ones in portions only, whereby the physical properties of the final products may be modified within wide limits. These compounds for instance may be condensed together with aldehydes and resin-forming amides like urea, thiourea, dicyandiamide and heterocyclic polyvalent amino compounds, for instance di- and triamino triazines. Polyfunctional amidines with at least two exchangeable hydrogen- or -nitrogen atoms may be condensed or pressed into resins directly with compounds splitting off aldehyde like formaldehyde, p-formaldehyde, hexamethylenetetramine and the like.

Example I

ϵ -caprolactam is transformed in benzene solution (3 volume parts benzene to 1 volume part lactam) by boiling for 6 hours with the equivalent amount of dimethylsulfate into the methylsulfuric acid salt of the lactim methyl ether, which is slightly soluble in benzene. The benzene solution, which does not contain a precipitate, is discharged into a 50 per cent potassium carbonate solution, which is in excess and covered with a layer of ether, thus liberating the lactim ether. It is obtained by fractional distillation of the dried benzene-ether layer in good output as colorless, terpene-like smelling liquid (b. p. 4 50–52°C).

Two mols lactim ether are dissolved in the same volume of alcohol and mixed with one mol hexamethylenediamine. After staying over night it is heated some more hours on the water bath and then the alcohol is distilled off. The remaining product is condensed with the equivalent amount of sebacic acid or adipic acid into a hard artificial material which may be spun from the melt.

The condensation proceeds very smoothly at temperatures between 220 and 260° C, as disturbing, volatile ingredients are practically not formed.

Instead of the free amidines the dihydrochloride is obtained, if the hexamethylenediamine is substituted by the dichlorid hydrate. The hydrochloride, very easily soluble in chloroform and alcohol, is precipitated by dried ether in the form of colorless crystals.

Similar divalent amidines as with hexamethylenediamine are obtained, if the lactim ether is caused to react with the calculated amounts of ethylene diamine, putrescine or symmetrical dimethylhexamethylenediamine.

Example II

From the lactim ether of the ϵ -caprolactam obtained according to Example I a product is obtained directly condensable into polyamide by heating at 200–260°C, if two mols lactim ether are mixed with one mol hexamethylenediamine-adipic acid salt in hot alcoholic solution, the mixture then heated for several hours at 100°C, the alcohol then distilled off and the condensation is carried through at 220–260°C. Finally also two mols of the lactim ether and one mol salt may be gradually heated at 200–220°C in a silver plated autoclave without a solvent, the pressure be relieved and the condensation be finished at 220–250°C.

Example III

The lactim methyl ether from ϵ -amino caprolactam is heated with one mol 5-aminohexanol-1 and the reaction product heated with the equivalent amount β -methyl adipic acid at 150–250°C in a nitrogen atmosphere first for 6 hours under atmospheric pressure, then for 6 hours in a high vacuum (about 1 mm). A relatively soft product which may be drawn into filaments is obtained.

Example IV

The 5-aminohexanol of Example III is substituted by the equivalent amount of 5-aminoamylmercaptane. The mercaptoamidine is condensed into a resin with formaldehyde in the presence of formic acid or oxalic acid.

Example V

The lactim methyl ether from ϵ -caprolactam is left over night with the equimolecular amount 6-aminohexane acid nitrile in alcoholic solution by adding 1/100 mol hydrochloric acid to 1 mol lactim ether and then (after 16 hours) heated on a steam bath for still a certain while. The reaction product remaining after the distillation is condensed by heating at 225–230°C in the presence of water in a sealed vessel into an artificial material, which may be spun from the melt after the pressure is relieved and the mass further heated for several hours at 250°C. The substance melts at about 208°C.

Example VI

The lactim methyl ether from 4-methylcyclohexanone-isoxime (mixture of 2 stereoisomers) is condensed with the equimolecular amount diethylene triamine. The reaction product gives a basic synthetic resin when heated with aqueous formaldehyde in the presence of acetic acid, which is used as auxiliary agent for dyestuff purposes.

Example VII

The benzene sulfo ester of the enolic ϵ -caprolactam is stirred while cooling into an alcoholic solution containing an excess of hexamethylenediamine. The reaction product presents a mixture, partly neutralized by benzene sulfo acid, consisting of the symmetrical hexamethylenediamidine, hexamethylenediamine and a compound obtained by reaction of 1 mol hexamethylenediamine and 1 mol lactim ester. The mixture may be directly used for the production of artificial materials by condensing with a dicarboxylic acid approximately corresponding to the amount of basic substances. The excess of hexamethylenediamine may be removed from the mixture of the free bases by distillation. The benzene sulfo ester is obtained by a reaction of the lactam with the sulfo chloride while sufficiently cooling in the presence of a tertiary base like pyridine.

Example VIII

1 mol piperidon is transformed in the presence of pyridine with propane sulfo chloride into the lactim sulfo ester. By the reaction of the ester with a solution of sodium butylate in *n*-butanol there is obtained the lactim butyl ether which is distillable without decomposition in the vacuum. By heating of the lactim ether with half the equivalent of water-free ethylenediamine at 140°C a reaction product by cleavage of butanol is obtained being condensable with formaldehyde into an artificial product capable of absorbing dyestuffs.

Similar products are obtained, if instead of the lactim ether from piperidon the α -thiopiperidon or its *S*-alkylethers are caused to react with the diamines.

PAUL SCHLACK.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF HYDROCARBON-CHLORIDES WITH 4 CARBON ATOMS FROM TRICHLORETHYLENE

Josef Wimmer, Muckenberg District of Liebenwerda, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 18, 1940

This invention relates to a process for polymerizing trichlorethylene as set forth in the patent 2,161,078 and in the patent application S. N. 283,456 and has for its object to provide an improved process for this purpose.

According to the methods of the forenamed patents the production of hexachlorbutene and pentachlorbutadiene is executed by heating trichlorethylene in an autoclave and in a discontinuous manner. The disadvantages of the discontinuous method of working at operations on a large scale (wholesale trade) are especially great at a process being executed under pressure and at high temperature, because on the one hand the arrangement of large autoclaves demands much material and costs and extensive safety devices and because on the other hand the attendance before all the filling up every time, the heating up to the high reaction temperature, the cooling down, the release and the emptying of the autoclave—is difficult, demands plenty of time and has considerable loss of warmth in consequence.

Now there was found, that the conversion of trichlorethylene into the hydrocarbon-chlorides can be continuously executed whereby a small pressure apparatus easily to be served can be used. Though the polymerisation of the trichlorethylene is a reaction proceeding relatively slowly, the trichlorethylene polymerizes surprisingly also in a satisfactory extent, if it is continuously pressed through a vessel, resistant to pressure and heated to the reaction temperature. A suitable pressure vessel is a tube, through which by a pump or by a pressure bulb the trichlorethylene is pressed through continuously and equally. The velocity with which the trichlorethylene converses in this pressure vessel, and with which it can be passed through correspondingly depends on the temperature and the purity of the trichlorethylene and that of the apparatus. The conversion proceeds under 200° still very slowly, with increasing temperature however the reaction velocity increases very much. About 250° were found as a generally suitable temperature, because at this temperature a sufficient reaction is obtained and the material of the wall of the vessel is unimportantly corroded. But also above this temperature till about 300° can be worked very well. Suitable materials for the inner wall of the vessel resp. for its lining are lead, nickel, silver, enamel. The pressure in the reaction vessel is suitably held on about 20 atu. Sometimes the technical trichlorethylene or the parts of the pressure apparatus, being in contact with it, contain organic or inorganic contaminations,

having the effect of splitting off HCl or inhibit the polymerization. If adding small quantities of the substances named in the patent application S. N. 283,456 it is possible to reduce the splitting off of HCl from the polymerization product to a low degree and to make inactive the catalysts which inhibit the polymerization.

The continuous process can also be executed in this way, that the polymerized trichlorethylene is wholly or partly splitted in pentachlorbutadien and hydrogen chloride, if the trichlorethylene is mixed with a small quantity of iron chloride and is pressed through the pressure tube in this way. At the high reaction temperature a small quantity of ironchloride is sufficient to obtain a nearly quantitative splitting off of HCl. But it is absolutely to avoid that the quantity of ironchloride which has proved as sufficient for the completely splitting off of HCl is exceeded because with increasing content of iron a delay of the trichlorethylene-polymerization enters, which primary proceeds. The quantity of ironchloride which is to add changes in the course of the reaction, because on the one hand a part of the added ironchloride is made inactive by contaminations in the trichlorethylene and in the apparatus and because on the other hand one part of the added ironchloride always remains in the reaction apparatus. The reaction can also be executed in the presence of a catalyst like superoxides.

Example 1

Through a heated, with lead lined tube of 1 m length and 5 cm wideness 3 l trichlorethylene to whom 1 drop of pyridine was added, were led pro hour. The temperature was in the middle of the tube 260°. The pressure was held on about 20 atu. The reaction product was cooled when leaving the tube and led off by a valve of release in a state cooled. The so obtained reaction product contained about 55% of unchanged trichlorethylene and about 45% of high boiling hydrocarbon-chlorides. In the latter constituent were contained about 92% of hexachlorbutene, about 6% of pentachlorbutadien and 2% of compounds, which could not be distilled. The splitting off of HCl corresponded approximately with the present pentachlorbutadien and was about 1.3 mol. pro hour.

Example 2

Through the same tube—according to the method of working described in example 1 3 l of trichlorethylene—to whom 0.02 g of ironchloride pro liter trichlorethylene were added—were

pumped through per hour. The temperature was 240°, the pressure was also held on about 20 atu. The obtained product contained on average 60% of unchanged trichlorethylene and 40% of high boiling hydrocarbon-chlorides, consisting of about 90% of pentachlorbutadien, of 8% of hexachlorbuten and of 2% of higher molecular compounds. At the same time a quantity of HCl was obtained

corresponding with the formed pentachlorbutadien. Continuously working, the quantity of ironchloride was diminished, when the velocity of polymerization decreased, on the other hand more ironchloride was added, when the decomposition of hexachlorbuten sank below 90°.

JOSEF WIMMER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR CONDENSATION OF PRIMARY ALIPHATIC ALDEHYDES

Hans Machemer, Burghausen, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed May 18, 1940

The invention refers to the production of glycoles and glycolic esters by condensation of aliphatic primary aldehydes with 3 till 6 carbon atoms.

There was found that carbides of the alkaline-earth metals per se or with oxydes of the alkaline earth metals resp.—hydroxides are excellently suitable as condensation agents. This fact is surprising, because milk of lime is known as condensation agent little suitable for the substituted aldehydes. During the reaction, according to the invention, indifferent solvents can be present, but it is not always necessary to use them. Also it is not out of question to carry on the process at over- or underpressure. There is no need of taking always pure aldehydes for starting materials. Suitable initial substances are also such, as they often fall on in the industry, which contain water and/or acids or compounds reacting like aldehydes.

If going out from aldehyde mixtures, corresponding mixtures of glycole half esters resp. glycoles are obtained. The half esters, being formed during the reaction cannot always be isolated, because they are occasionally saponified by the alkaline reacting condensation agent being present and especially—when water is present—in the leap of the reaction mixture so that 1,3-glycole and aliphatic carbon acids are obtained as the end product. The reaction is mostly done at boiling temperature under reflux but there can be worked also at lower temperatures, if more time is spent.

In the industry the process is mostly executed so, that the mixture of the starting materials is stirred with the condensation agent in the warmth and in a stirring apparatus—suitable supplied with a reflux condenser—till to the end of the condensation. It is also possible, to lead the starting materials by repumping continually over the condensation agent, f.e. granulated calcium carbide, whereby an equal generation of acetylene has to occur. The working up of the reaction mixture usually is executed in vacuum, after having siphoned off the condensate and having isolated the oil, reserved in the carbide sludge by extraction or solution of the lime sludge in cold diluted acid. The 1,3-glycole half ester obtained according to the invention are used especially as softening agents and solvents in the lacquer-industry.

Example 1

100 parts of weight of anhydrous butyric aldehyde are boiled under reflux and stirring with 20

parts of calcium carbide for four hours and a half, whereby the temperature of reaction vessel increases to 140°. Thereby nearly 1 part of acetylene is formed. If the reaction product is worked up, there are obtained:

5 parts of a fraction containing 2-ethyl-3n-propyl-acrolein, 12 parts of 2-ethyl-n-hexandiol-(1.3), 63 parts of 2-ethyl-n-hexandiol-(1.3)-butyrate boiling at 143° at 1 mm ($D_{20}=0.943$) and 7 parts in residue.

Example 2

A mixture of 100 parts of butyric aldehyde, 2,7 parts of water and 1,7 parts of crotonic aldehyde is brought in contact—by repumping—with 9 parts of calcium carbide which contains 1 part of calcium oxyde. Hereby the temperature is increased from 50° to 130° C. During the condensation 3 parts of acetylene are generated. After having finished the reaction—that is when no more butyric aldehyde is present, the mixture is cooled down, acidified with hydrochloric acid and then fractionated under vacuum. There are obtained:

19 parts of 2-ethyl-3-propyl-acrolein, 5 parts of 2-ethyl-hexandiol-(1.3) and 37 parts of 2-ethylhexandiol (1.3)-butyrate.

Example 3

100 parts of butyric aldehyde containing 0,5% of water are boiled with a mixture of 5 parts of calcium carbide and 0,05 parts of barium oxyde for 5 hours under reflux, whereby the temperature increases to 120°. During the fractionation under vacuum 15 parts of 2-ethyl-3-propyl-acrolein pass over. The contents of the reaction vessel is saponified with sodium lye, whereby 41 parts of 2-ethylhexandiol-(1.3) boiling at 132° at 11 mm ($n_{D,20}^2=1.453$, $D_{20}=0.935$) and 22 parts of butyric acid are obtained.

Example 4

100 parts of technical capronic aldehyde, which contains small quantities of caproic acid and about 0,6% of water are heated with 20 parts of calcium carbide for four hours till about 110°, whereby 3 parts of acetylene gas are generated. After having precipitated the mixture is filtered and the turbid solution containing calcium oxide is fractionated under vacuum. There are obtained until boiling at 121° at 6 mm 40 parts of 2n-butyl-3-n-amyl-acrolein and 2n-butyl-3n-amyl-propyl-alcohol and the caproic acid ester of it; boiling at 135–153° at 1 mm 10 parts of 2n-butyl-3n-amyl-allyl alcohol besides 35 parts of residue.

Example 5

100 parts of isopropyl-acetaldehyde are condensed at boiling temperature under reflux for about 3 hours in the presence of calcium carbide. There are obtained 29 parts of half ester boiling at 130–170° at 16 mm, which yields 2-isopropyl-3-isobutyl-propandiol-(1.3) boiling at 130° at 12 mm, if saponified.

Example 6

100 parts of butyric aldehyde, containing 0.5% of water are heated with 50 parts of xylene and 15 parts of calcium carbide under stirring for 8 hours till about 110°. Thereby 4 parts of acetylene are generated. When the oil, decanted from the sludge of carbide, is fractionated, there are

obtained: 5 parts of butyric aldehyde, 14 parts of 2-ethyl-3-propyl-acrolein and 38 parts of 2-ethyln-hexandiol-1.3-butyrate.

Example 7

100 parts of propionic aldehyde are boiled with 5 parts of calcium carbide for 6 hours under reflux. Then the mixture is distilled whereby 12 parts of methyl-ethyl-acrolein pass over. The residue consists in the main point in 2-methylpentandiol-1,3-propionate boiling at 120–125° at 15 mm. The ester is saponified with an excess of sodium lye, whereby 34 parts of 2-methylpentandiol-1,3 boiling at 100–105° at 15 mm and 18 parts of propionic acid are obtained.

HANS MACHEMER.

ALIEN PROPERTY CUSTODIAN

POLYMERIZATION PROCESS

Herbert Berg, Burghausen, Oberbayern, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 27, 1940

This invention relates to the polymerization of vinyl acetate; more particularly, it is directed to certain improvements in the preparation of vinyl acetate polymers whereby the characteristics of the polymeric products obtained are modified and the procedural steps involved are simplified.

It has been known heretofore that vinyl acetate may be polymerized by the action of heat and/or pressure and/or actinic radiation, and that the polymerization may be accelerated by the addition of polymerization catalysts, of which the most important are inorganic peroxides, such as hydrogen peroxide and per salts, and organic peroxides such as benzoyl peroxide.

It is also known that a number of chemical agents, of which hydroquinone and nitrobenzene may be mentioned as typical, exert an inhibiting action on the polymerization of vinyl acetate. It has been a common practice to add polymerization inhibitors of this character to monomeric vinyl acetate in order to prevent polymerization during storage, the inhibitors being eliminated by fractional distillation or other means prior to carrying out the polymerization operation.

I have now discovered that agents generally known to be polymerization inhibitors, when added to vinyl acetate in very minute proportions, produce an entirely different effect than that produced by the addition of these agents in the usual inhibiting amounts. When added in the very small proportions contemplated by the present invention, I have found that these agents do not function to inhibit polymerization materially, but in many cases actually serve to promote it substantially. Thus, by the proper selection of the inhibitor and the quantity of it used, it has been found that the induction period usually required for the polymerization to start, and the total time required for completion of the polymerization, can be appreciably shortened. This results in savings in heat requirements and labor and supervision costs, and in an increase in the productive capacity of the manufacturing equipment. Moreover, in certain instances, smaller amounts of the polymerization catalyst may be used than in the usual polymerization method, with corresponding savings in catalyst costs. Perhaps the most important advantage of the new method, however, resides in the fact that the characteristics of the polymeric products are substantially modified by the presence of the addition agents and it is thus possible to produce products having certain special properties which are not obtainable by methods heretofore known.

In carrying out the polymerization of vinyl acetate in the presence of polymerization inhibitors in accordance with the present invention, any of the usual polymerization procedures known to the art may be employed. Solvents for the monomer and/or polymer may be present or absent, and the polymerization may be effected by the action of actinic light by heat, preferably promoted by the action of polymerization catalysts. The present invention, however, has special advantages as applied to the so-called emulsion polymerization method wherein the monomeric vinyl acetate is emulsified in a non-solvent medium and then polymerized to form a latex-like emulsion of the polymer. An aqueous medium containing a partially saponified polyvinyl acetate having a saponification number of 80 to 180 and preferably from 120 to 130, as an emulsifying agent has been found to be a particularly satisfactory medium for this purpose although, of course, other media and emulsifying agents may be used. By the addition to the vinyl acetate of minute amounts of polymerization inhibitors there is effected a considerable reduction in the particle size of the emulsified polymer for a given concentration of emulsifying agent. This makes it possible to prepare latex-like emulsions of high stability even though relatively small amounts of emulsifying agent are used. Similarly, the addition of polymerization inhibitors in accordance with the present invention may be used to advantage in the so-called granular dispersion method of polymerization, wherein the monomeric vinyl acetate, instead of being emulsified, is dispersed in an aqueous medium in the form of macroscopic discrete particles and maintained in dispersion by agitation until polymerization is completed; thereupon stirring is stopped and the polymerization product is precipitated in the form of granules or globules. By the addition of small amounts of polymerization inhibitors to vinyl acetate polymerized in this manner, it has been found that the resultant product is in a more finely divided state than otherwise would be obtained.

In addition to hydroquinone and nitrobenzene, mentioned above, there are a number of other polymerization inhibitors which, when used in less than a polymerization-inhibiting amount, produce the advantageous action upon the polymerization process and products which have just been described. Among these agents may be mentioned salicylic acid, p-amino-phenol (Methylol), hexadienal, phenol, cresol, resorcinol, pyrocatechol, pyrogallol, pyridine, quinoline, ani-

line, naphthylamine, p-nitroaniline, triethanolamine, diethylamine, hydrazine hydrate, benzaldehyde, acetophenone, tannin, urea, carbon disulfide, hydrogen sulfide and sulfur dioxide. The foregoing list of agents is not to be regarded as exhaustive, since I have found it to be a general rule that any agent which is capable of inhibiting polymerization in relatively substantial proportions is effective for producing the results of the present invention when used in proportions insufficient to substantially inhibit polymerization. It will be obvious to those skilled in the art that other compounds may be used for the same purpose and the suitability of any compound for the purpose may be easily determined by simple test.

The invention may be illustrated by the following examples:

Example I

A mixture of 100 cc. of vinyl acetate, 1.0 mg. of nitrobenzene and 0.36 gram of technical benzoyl peroxide was heated under a reflux condenser to a temperature of 70° C. The polymerization reaction, as manifested by vigorous boiling of the vinyl acetate, began after an induction period of about 11 minutes; after an additional period of 2½ hours the vinyl acetate was practically quantitatively polymerized to a solid block. The polymerization product, when dissolved as a 20% solution in ethyl acetate, had a viscosity of 40 seconds as measured by the Hercules Powder Company method. A 20% solution of the product in vinyl acetate had a viscosity of 50 seconds, as determined by the same method.

By the polymerization of vinyl acetate under the same conditions, but without the addition of nitrobenzene, the polymerization begins after an induction period of 15 to 20 minutes and requires four to five hours at a temperature of 74 to 76° to go to completion. The viscosity of a 20% solution of the product will range from about 100 to 150 seconds.

By increasing the amount of nitrobenzene utilized in the foregoing procedure from 1.0 to 2.5 mg., about 30 minutes is required for the polymerization to begin but it is completed after an additional period of only about 2¼ hours. A 20% ethyl acetate solution of the polymer thus obtained has a viscosity of 28 seconds while a corresponding vinyl acetate solution has a viscosity of 35 seconds.

By increasing the amount of nitrobenzene originally present to 15 mg., the polymerization begins at a temperature of 76° C., after an incubation period of 6 hours, but the polymerization is completed after an additional 3½ hours. A 20% solution of the polymer in ethyl acetate has a viscosity of 4.4 seconds and a 20% solution in vinyl acetate a viscosity of 5.5 seconds.

Example II

100 cc. of vinyl acetate containing 0.5 mg. of hydroquinone and 0.36 gram of benzoyl peroxide was polymerized in accordance with the procedure described in Example I at a temperature of 72° C. The polymerization initiated after a period of 15 minutes was complete after 4 hours. A 20% solution of the polymer in ethyl acetate had a viscosity of 244 seconds and a 20% solution in vinyl acetate had a viscosity of 305 seconds.

Example III

By carrying out Example I, but utilizing 0.5 mg. of hydrazine hydrate as the polymerization inhibitor, the induction period was 10 minutes

and the polymerization period 3½ hours. The polymerization product had a viscosity of 756 seconds in 20% ethyl acetate solution and 945 seconds in 20% vinyl acetate solution.

Example IV

Utilizing 0.5 mg. of diethylamine as the polymerization inhibitor in the process of Example I resulted in an induction period of 10 minutes, a polymerization period of 2½ hours and a viscosity of 10.5 seconds for a 20% ethyl acetate solution of the product and 13.1 seconds for 20% vinyl acetate solution of the product.

Example V

Utilizing 0.5 mg. of p-amino-phenol (Metol) as the polymerization inhibitor in the procedure of Example I, the induction period was 10 minutes, the polymerization period was 1½ hours and the viscosities of the product were 75.0 and 93.7 seconds for 20% ethyl acetate and vinyl acetate solutions, respectively.

Example VI

Utilizing 0.5 mg. of salicylic acid as the polymerization inhibitor in the process of Example I, the induction period was 5 minutes, the polymerization period was 3 hours and the viscosity of the product was 208 and 250 seconds in 20% ethyl acetate and vinyl acetate solution, respectively.

Example VII

Using 0.5 mg. of cresol as the polymerization inhibitor in the procedure of Example I, the incubation period was 20 minutes, the polymerization time 2½ hours and the viscosity of the product in 20% vinyl acetate solution about 1000 seconds.

Example VIII

Utilizing 0.5 mg. of pyrogallol as the polymerization inhibitor in the process of Example I, the induction period was 20 minutes, the duration of the polymerization reaction 3 hours, and viscosities of 20% solutions of the product in ethyl acetate and vinyl acetate, respectively, 382 and 478 seconds.

Example IX

Utilizing 0.5 mg. of acetophenone as the polymerization inhibitor in the process of Example I, the induction period was 15 minutes, the polymerization period was 3 hours and the viscosities of 20% solutions in ethyl acetate and vinyl acetate, respectively, were 817 and 1021 seconds.

Example X

Utilizing 0.5 mg. of hexadienal as the polymerization inhibitor in Example I, there was an induction period of 12 minutes, a polymerization period of 2 hours and the viscosities of the product were 900 and 1125 seconds for 20% solutions in ethyl acetate and vinyl acetate, respectively.

Upon increasing the amount of hexadienal to 2.5 mg., the induction period was 40 minutes, the polymerization period was 2½ hours and the viscosities of the product were 127.5 and 159.8 seconds for 20% ethyl acetate and vinyl acetate solutions, respectively.

With 5 mg. of hexadienal, the induction period was 45 minutes, the polymerization period was 2½ hours and the respective viscosities 33 seconds and 41.2 seconds.

By the addition of a combination of 0.5 mg. of hexadienal and 0.5 mg. of propionaldehyde the induction period was 15 minutes, the polymerization period was 2¼ hours and the viscosities of

the product were 2.0 seconds and 2.5 seconds, respectively, for 20% ethyl acetate and vinyl acetate solutions.

Example XI

The addition of 0.5 mg. of sulfur dioxide as the inhibitor in the procedure of Example I gave an induction period of 13 minutes, a polymerization period of 2½ hours and product viscosities of 11.4 seconds for 20% ethyl acetate solution and 14.2 seconds for a 20% vinyl acetate solution.

Example XII

The addition of 0.5 mg. of hydrogen sulfide as the polymerization inhibitor in the procedure of Example I gave an induction period of 5 minutes, a polymerization period of 2 hours and a product viscosity of 750 seconds for the 20% ethyl acetate solution and of 937 seconds for the 20% vinyl acetate solution.

Example XIII

Crude vinyl acetate to which had been added hydroquinone in the proportion of 20 grams per 100 kgs. of vinyl acetate was carefully fractionated, to produce a pure vinyl acetate. Two hundred and fifty kilograms of vinyl acetate thus obtained was emulsified in the cold in 400 kgs. of a 10% aqueous solution of a water-soluble partial acetate of polyvinyl alcohol (saponification number 120 to 130). To this emulsion was added 400 cc. of concentrated hydrogen peroxide solution and the emulsion then heated to a temperature of 60–61°C., whereupon polymerization began to take place. The reaction then proceeded without further heating. During a period of several hours an additional 550 kgs. of vinyl acetate and 510 kgs. of cold water were added to the reaction mixture. From time to time, whenever the reaction gave evidence of subsiding, further amounts of concentrated hydrogen peroxide solution were added, the total amount required being approximately 700 cc. As the reaction proceeded the temperature was allowed to rise until it reached approximately 85 to 90°C. at the conclusion of the polymerization. Practically quantitative conversion of the vinyl acetate to the polymer was secured after a period of approximately 8 hours. The polyvinyl acetate emulsion thus obtained had a viscosity of 127 seconds as measured by the Hercules Powder Company method. It had a settling number of 3.6, the settling number being an indication of the particle size and being determined by diluting 1 cc. of the emulsion with water to a volume of 100 cc. and measuring the amount of material settled out during a settling period of 90 minutes.

By carrying out the foregoing procedure without adding hydroquinone to the crude vinyl acetate prior to fractionation, the polymerization was completed in 7 hours and the emulsion had a viscosity of only 45 seconds. The settling number was 10, indicating that the emulsified particles were considerably larger in size than those obtained with vinyl acetate containing hydroquinone.

By repeating the foregoing procedure, with the exception that crude vinyl acetate containing 10 grams of hydroquinone per 100 kgs. of crude

vinyl acetate was subjected to steam distillation prior to polymerization, the polymerization under the same conditions took place in 9 hours and a polyvinyl acetate emulsion having a viscosity of 470 seconds and a settling number of 2.5 was obtained. In this case the distilled vinyl acetate contained a larger percentage of hydroquinone due to the fact that the latter was partially volatilized during the steam distillation.

Starting with 800 kg. of pure vinyl acetate containing 10 grams of hydroquinone, polymerization under the conditions described above was completed after 15 hours and a polyvinyl acetate emulsion with a settling number of 1.1 and a viscosity exceeding 1000 seconds was obtained. The emulsion was of a pasty consistency and its viscosity could be increased even further by the addition of plasticizers. Even upon reducing the hydroquinone content to as low as 5 grams per 800 kgs. of pure vinyl acetate it is still possible to obtain pastes or emulsions of any desired consistency in which the particle size is exceedingly small and which are of excellent stability.

As indicated by the foregoing examples, by suitable selection of the polymerization inhibitor and the quantity used, it is possible to vary the degree of polymerization within wide limits. Furthermore, the particle size of the polymer emulsions can be reduced to a surprising extent and at the same time a considerable saving in the amount of emulsifying agent used be effected.

It is to be noted that all polymerization inhibitors do not function in precisely the same manner; accordingly, the selection of the particular inhibitor will depend upon the results desired in each case. For example, salicylic acid and p-amino-phenol are particularly useful in accelerating the rate of polymerization; other inhibitors such as, for example, cresol and hexadienal, function primarily to increase the viscosity of polymer emulsions. In case of hexadienal, as is indicated by Example X, it is possible to regulate the degree of polymerization of the product over an exceedingly wide range by suitably adjusting the proportion of hexadienal added. It is advantageous in certain instances to combine two or more polymerization inhibitors in order to obtain a desired combination of properties in the polymerized product.

It may be noted that the polymerization inhibitors of the present invention may be utilized in polymerization inhibiting amounts for stabilizing monomeric vinyl acetate while in storage. When it is desired to subject the stabilized monomer to polymerization, it may be distilled under carefully controlled conditions so that the inhibitor is incompletely removed and only that amount which is required for the desired modification of the polymerization process will remain.

It is to be understood that the invention is not restricted to the specific illustrative embodiments thereof described hereinabove, but includes all such variations, modifications and equivalents as fall within the scope of the appended claims.

HERBERT BERG.

ALIEN PROPERTY CUSTODIAN

PROCESSES OF PRODUCING NON-YELLOW-
ING PHENOL-FORMALDEHYDE CONDEN-
SATESBernhard Habraschka, Hamburg, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 27, 1940

This invention relates to a process of producing non-yellowing phenol-formaldehyde condensates.

Commercial phenol-formaldehyde condensation products as well as varnishes made therefrom are open to the objection that they turn yellow or brown within a relatively short time.

To diminish this tendency it has been proposed to add metallic oxides or urea-formaldehyde condensates, but such additions while delaying yellowing do not eliminate it. At any rate, fastness to light cannot be attained this way.

It is generally known that phenol cannot be completely converted when condensed with formaldehyde. Finished condensates always contain therefore greater or smaller amounts of free phenol, and it could be ascertained that phenol-formaldehyde condensates turn yellow only in the presence of free phenol. Yellowing always occurred through the action of ultraviolet rays, through oxidation during exposure to air or as a result of heat, and decomposition of the resin molecule was also noted.

It has now been found that yellowing or discoloration of phenol-formaldehyde condensation products, even when subjected to the action of ultraviolet rays, oxygen or heat, can be avoided by converting, in the course of the reaction, the free phenol contained therein into a neutral phenol compound with the aid of an active reagent. In this manner it becomes possible to stabilize phenol condensates and to obtain products that are fast to light.

For example, excellent results could be secured by adding a synthetic fatty acid of the oxidation of paraffin or the esters thereof, the most favorable effects being produced by the C_9-18 fatty acids or their esters.

The formation of phenolates, combined with fatty acid, of the paraffin group produces also, besides the advantages mentioned, stabilization to such a degree that decomposition of the resin molecule does not occur any more.

The process according to the invention is carried out by dissolving the phenol-formaldehyde condensate, prepared in known manner, in a solvent preferably comprising a mixture of two or more parts of ethyl alcohol, butyl alcohol, propyl alcohol and the ester and homologue of benzene. A reagent of the kind mentioned is then added to the dissolved product which is finally hardened in known manner.

The following examples indicate a suitable manner of performing the process according to the invention:

Example 1

100 parts (meta-para- or ortho-) phenol-formaldehyde condensate are dissolved in 100 parts of a solvent mixture comprising 75 parts ethyl alcohol, 10 parts butyl alcohol, 10 parts

ethyl glycol and 5 parts toluene. To the resin solution 1 to 10 parts, or more if necessary, of a synthetic fatty acid, preferably one of the C_9-C_{18} fatty acids, of the paraffin oxidation are added. The mixture is then mixed with .1 to 10% hydrochloric or sulfuric or phosphoric or boric acid or active organic chlorine or sulfo compounds and hardened at room temperature.

Example 2

100 parts (meta-para- or ortho-) cresol-formaldehyde condensate are dissolved in a solvent mixture comprising 30 parts ethyl alcohol, 30 parts butyl alcohol, 20 parts propyl alcohol and 20 parts toluene and mixed with 1 to 10 parts, or more if necessary, phthalate ester of a fatty acid of paraffin oxidation. This mixture is then mixed with .1 to 10% hydrochloric or sulfuric or phosphoric or boric acid or active organic chlorine or sulfo compounds and hardened at room temperature.

The resulting products yield almost transparent solutions and final products of equal clearness.

To increase elasticity known substances, as condensation products of the vinyl group, may be added to the mass.

Products of equal composition and prepared in the same manner except that synthetic fatty acids were omitted or replaced by an addition of 1 to 10 parts of a urea-formaldehyde condensate failed to show fastness to light. A product without a synthetic fatty acid constituent yellows relatively quickly and even turns brown after a few weeks, whilst the addition of a urea-formaldehyde condensate slightly delays yellowing which occurs, however, after several weeks and, in certain instances, leads to browning. Higher additions of urea-formaldehyde condensate amounting for instance to 20% of the phenol-formaldehyde condensate are practically impossible, since due to the catalytic influence of the contact substances rapid hardening occurs already in the solution. The dissolved substances used in the preparation will keep about one hour, but an addition of 20% urea-formaldehyde condensate is not sufficient to prevent or effectively decrease yellowing.

When .01 to 5% of the salts of the zinc or tin and bismuth or vanadium group are added instead of urea-formaldehyde condensates, yellowing is retarded and, if the corresponding chlorine compounds are used, will occur only after weeks or months, though it cannot be avoided in the long run.

Phenol-formaldehyde condensates treated according to the invention do not show, on the other hand, any yellowing or discoloration, even if strongly acted upon by heat, oxygen and ultraviolet rays, and are practically absolutely fast to light.

BERNHARD HABRASCHKA,

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF KETO-ALCOHOLS

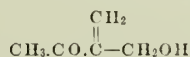
Giulio Natta, Milano, Italy; vested in the Alien Property Custodian

No Drawing. Application filed June 12, 1940

It is known that by reacting ketones with formaldehyde, keto-alcohols may be obtained but all the processes disclosed in the biography do not allow the obtention of higher yields and pure products.

In fact by condensation in the presence of basic substances, other products other than keto-alcohols are formed, i. e. from acetone are obtained diacetone-alcohol, phorone and homologues, formoses and further products of condensation or resinification. In order to lower the formation of resins, somebody has suggested to operate in the presence of a great excess of ketone, but in such conditions the formation of products of polymerization of ketones and other secondary reactions may not completely be avoided.

By the present invention it is instead possible to obtain keto-alcohols with an high yield. E. g. starting from acetone, keto-butanol 3.1 (known also under the name of acetoethyl alcohol or methoxy ethylketone) $\text{CH}_3\text{CO}\cdot\text{CH}_2\text{CH}_2\text{OH}$ may be obtained with a practically quantitative yield. The same process, when effected by the use of greater proportion of formaldehyde as will thereafter be disclosed, allows the obtention of methylenketobutanol (2 methylen-3.1.ketobutanol)



instead than ketobutanol 3.1.

The process is effected by employing a diluted aqueous solution of ketone and formaldehyde in the presence of a given concentration of hydrogen ions and within given intervals of temperature.

The pH of the solution must be kept during the condensation below 10 and preferably between 8 and 9. For lower concentrations of hydrogen ions secondary reactions are developed; while for higher concentrations the reaction becomes very slow.

The temperature must be kept below 50°C and when it is desired to obtain only keto-butanol by condensation of acetone with formaldehyde it is convenient that the same be kept between 25°C and 32°C, while it may preferably be kept between 35°C and 40°C when it is desired to obtain methylenketobutanol.

Under this conditions it is possible to operate with equimolecular concentrations of acetone and formaldehyde, but a slight excess of acetone is not harmful as it may be completely recovered. Even when operating with equimolecular concentrations secondary reactions are practically eliminated. In the presence of an excess of formaldehyde till a proportion of 2 molecules to 1 mole-

cule of acetone and for slightly higher temperatures, the reaction proceeds with formation of methylenketobutanol, but also under these conditions the formation of resins and other secondary reactions is eliminated.

The concentration of the aqueous solution of acetone may vary within broad limits and e. g. it may range between 30% to 70% when operating with a solution of formaldehyde at 30%+40%. It could also be possible to operate with more diluted solutions but practically, in order to shorten the time of reaction, it is convenient to operate with concentration of acetone at about 50%.

Of no importance is the nature of the condensation medium (soda, potash, magnesia, lime, borax, a.s.o.), provided that substances which do not readily react with aldehyde and acetone be used and the pH value results between the above mentioned limits.

The speed of reaction depends exclusively on the concentration of the oxidriles ions and on the temperature; when operating with a pH between 8.5+9 and at 30°C, the reaction is completed in about 4 hours.

By slightly increasing the temperature, the reaction is more rapid but small quantities of methylenketobutanol are formed. Methylenketobutanol is prevalent also when, besides than operating at a higher temperature, an excess of formaldehyde is used.

When condensation is completed the solution is neutralised and the separation by distillation of ketoalcohols from water may be carried out. After elimination of water, the vacuum distillation may be effected and e. g. ketobutanol and methylenketobutanol completely distill without leaving any residue.

Without further treatment and purification the neutral or acid solution of ketobutanol and methylenketobutanol may be hydrogenated into butylenglycol 1.3 and 2. methylbutylenglycol 1.3 respectively.

The mentioned process may be of importance in the manufacture of synthetic rubber for the fact that butylenglycol 1.3 gives, by dehydration, as known, butadiene and methylbutylenglycol gives, even by dehydration, isoprene.

The same processes may also be of interest in the manufacture of explosives for the fact that glycols obtained by reduction of ketoalcohols may give by nitration nitric esters which possesses very interesting properties as explosives.

Other higher ketoalcohols supply the corresponding glycols.

GIULIO NATTA

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF BUTADIENE FROM BUTANE OR BUTANE CONTAINING GASES

Giulio Natta, Milano, Italy; vested in the Alien Property Custodian

No Drawing. Application filed June 12, 1940

It is known that by the catalytic dehydrogenation of butane, gases containing butylene and butadiene are obtained.

It is also known, as disclosed in a prior Patent by the same Applicants, that the best yields in the dehydrogenation of butylene into butadiene are obtained when working in the presence of carbon dioxide.

When, however, butane is used as a starting material it is very difficult to directly obtain a high yield of transformation in butadiene, except when working at very high temperatures at which, owing to secondary reactions, remarkable losses occur.

The reason of the low yield is due to the fact that, owing to the law of mass action, the hydrogen molecule which is formed in the dehydrogenation of butane into butylene opposes to the further dehydrogenation of butylene into butadiene.

A process whereby it is possible to obtain high yields in the transformation of butane into butadiene, would offer a remarkable interest owing to the important use that butadiene may find in the manufacture of polymers useful in the synthetic rubber industry.

By this invention it is possible to obtain high yields of transformation, preventing that a remarkable loss of substances in secondary reactions may occur.

This invention consists in the dehydrogenation of butane in the presence of carbon dioxide at relatively low temperatures e. g. $500^{\circ}\text{C} + 600^{\circ}\text{C}$.

Under these conditions the dehydrogenation is only partial, but losses owing to secondary reactions are avoided.

Afterwards, the reaction products, consisting of a gaseous mixture of: unaltered butane, butylene, butadiene, hydrogen, carbon dioxide, carbon oxide and water vapors, are cooled, eventually compressed, and both temperature and pressure respectively are fixed in a manner that practically all the butadiene, butylene and butane may separate in the liquid state, while hydrogen and carbon oxide separate in the gaseous state.

The carbon dioxide remains partially dissolved in the mixture of liquid hydrocarbons while partially remains in the residual gases and may eventually be separated from the latter and recovered by means of suitable solvents according to the known methods.

The mixture thus obtained consisting of butane, butylene and butadiene, eventually supplied with further carbon dioxide, is again passed at slightly higher temperatures (about $600^{\circ}\text{C} + 650^{\circ}\text{C}$) upon

a dehydrogenating catalyst, so that the butane still present and the butylene previously formed may be further dehydrogenated into butadiene.

When it is desired to obtain a mixture much enriched with butadiene, a third treatment may be effected after the new separation of hydrogen and other difficult condensable gases.

By this process it is possible to obtain a production of gases much enriched with butadiene which may directly be employed for the manufacture of polymers of butadiene or which may be utilized for the manufacture of pure butadiene e. g. by a fractionated absorption according to a prior patent by the same applicants.

In any case if butadiene is used in the manufacture of synthetic rubber by polymerization (e. g. with sodium or in emulsion e. g. with styrol), the butylenes and eventually the butane accompanying it and which do not polymerize, may after polymerisation be recovered as gases and treated again in order to be dehydrogenated into butadiene.

This process may be applied not merely to butane but also to mixtures of butane and butylene coming from the liquefaction and rectification of gases coming from the stabilisation of gasolines obtained by cracking or hydrogenation, or even to butylene resulting as a by-product in the manufacture of synthetic rubber or obtained by dehydration of butyl-alcohol.

Further, the process may be applied to the fraction C_4 obtained by distillation and rectification of hydrocarbons obtained from water gas through the Fischer's synthesis effected at temperature and pressure higher than the usual.

E. g. the hydrocarbons obtained by synthesis from carbon oxide and hydrogen by reaction upon catalysts made of cobalt at a temperature higher than 200°C , contain remarkable proportions (eventually higher than 20%) of butane and butylene. Said fractions, separated from the other hydrocarbons and dehydrogenated in the presence of carbon dioxide upon a dehydrogenating catalyst (e. g. consisting of reduced nickel on a backing or bentonite) according to the process disclosed may supply, after two or three treatments, a mixture enriched with butadiene which may be used in the manufacture of synthetic rubber. Thus it is possible to obtain about 30 grs. of butadiene from 1 cm. of water gas and further 100 grs. of hydrocarbons resulting as by-products in the synthesis of water gas after the separation of the fraction C_4 .

Said yields are of interest and afford to carry out the industrial production of synthetic rubber

using as a starting material water gas obtained from the gasyfication of poor fuels.

When the recovery of hydrogen coming from the dehydrogenation of butane is not deemed of interest, a small quantity of air or oxygen may eventually be added to the mixture of butane and carbon dioxide.

In such a case, by using catalysts affording the selective combustion of hydrogen, to which purpose the metals of the eighty group of the periodic system are capable of acting, the yield of each single operation of dehydrogenation may be improved and consequently by only one or two operations of dehydrogenation a product enriched with butadiene can be obtained.

The latter method must however be effected in

the presence of well determined quantities of air in order to avoid the formation of explosive mixtures or anyhow secondary reactions.

To said purpose the quantity of oxygen present in the mixture must be lower than that which is required for the complete combustion of the hydrogen coming from the dehydrogenation of butane into butadiene.

When butane is obtained from water gas by the Fischer's synthesis under a pressure of 10-20 atm., the dehydrogenation of butane may be effected by utilizing the carbon dioxide coming from the washing under pressure of the water gas in order to purify it from the carbon dioxide always therein present.

GIULIO NATTA.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF POLY- CONDENSATION PRODUCTS CONTAINING NITROGEN

Paul Schlack, Berlin-Treptow, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed June 19, 1940

This invention relates to the manufacture of nitrogenous polycondensation products.

By condensation of diisocyanates with glycols there are obtained high molecular polyurethanes which may be used, if the degree of polymerization is high enough, as starting material for formed structures, for instance fibers. Products of this kind which may be spun are for instance obtained by the reaction of octamethylene diisocyanate with 1,4-butanediol, according to U. S. patent application Ser. No. 239,456, filed November 8, 1938.

Similar products are formed if diurethanes, for instance hexamethylene-bis-carbamic acid diphenyl ester, are caused to react with glycols, for instance decamethylene glycol, according to U. S. patent application Ser. No. — (corresponding to the German patent application I. 64 524 IVc/12 o, filed May 6, 1939).

Also polyurethane compounds have already been produced from components, which, besides the urethane-forming groups, contain already amide groups (carbonamide groups, urea groups, sulfon amide groups, sulfamide groups) linked to the C-atoms with the carbonyl group in an open chain or in hetero-cyclic rings, according to U. S. patent application Ser. No. — (corresponding to the German patent application I. 64 650 IVc/12 o, filed May 17, 1939).

This invention has as an object the preparation of new and valuable compositions of matter, particularly synthetic fiber-for-fiber-forming materials.

A further object is the preparation of filaments, fibers and ribbons from these materials.

A further object is the manufacture of materials to be used for dye-casting, spraying and pressing of three-dimensional structures.

A further object is the manufacture of synthetic lacquers and waxes.

Still further objects will become apparent from the detailed specification following hereinafter.

It has been found that new and valuable nitrogenous poly-condensation products are obtained, if compounds of carbonic acid with amino alcohols or mercaptanes are intermolecularly condensed by heating, said amino alcohols and amino mercaptanes having amino- and hydroxyl- or sulfhydryl-groups (linked to saturated C-atoms) and possessing a chain of at least four C-atoms between the terminal amino nitrogen and the hydroxyl- or mercapto-group, if desired interrupted by hetero-atoms or -groupings like O, S, SO, SO₂, whereby in said carbonic acid compounds the carbonic acid radical is contained in

the form of an N-carboxylic acid-ester radical or -amide radical or an O-ester compound. This is accomplished, if desired, in the presence of solvents or diluents or of catalysts which favour the separation of ammonia or alcohol, especially catalysts adapted for the interchange of ester radicals like potassium-carbonate, magnesium oxide, magnesium methylate, hydrogen halide toluene sulfonic acid, camphor, sulfonic acid zinc chloride, stannous chloride.

Adapted for these condensations are not only the derivatives of simple amino alcohols, for instance derivatives of the 4-amino-butanol butanol, the 5-amino pentanol, the 4-amino cyclohexanol, the 4-amino butyl mercaptane (from benzoyl amino butyl chloride and potassium sulfhydrate with following hydrolysis), but also more complicated amino oxy- or amino mercapto compounds, the chain of which may be interrupted by hetero atoms or hetero groups like O, S, SO₂, for instance derivatives of the ω -amino butyl, ω' -oxy propyl sulfide (from benzoyl amino butyl mercaptane and 3-bromo propanol). There are included especially also such derivatives of amino oxy- or amino mercapto compounds, the chain of which is interrupted by amide groups, for instance by carbonamide groups linked to carbon, urea groups, sulfon amide groups, sulfamide groups. These amide groups may be contained in the open chain as well as in hetero-cyclic nuclei, inserted into the chain, or may be contained in both at the same time, according to U. S. patent application ser. No. — (corresponding to the German patent application I. 64 650 IVc/12, filed May 17, 1939).

A special form of application is the following: amino alcohols or their halides are caused to react with phosgene and the intermediate products are then advantageously heated in the presence of a diluent, whereby further condensation takes place by splitting off hydrogen halide. It is to be presumed that, with regard to the salts, chloroformic acid esters are first formed and then the chloride group reacts with the nitrogen, saturated by hydrogen halide, by splitting off two mols halogen halide. As solvents or diluents for the reaction there are especially suitable halogenated hydrogen-carbons with a boiling point between 110° and 170°C, for instance tetrachloroethylene, tetrachloroethane, chlorobenzene, o-dichlorobenzene. With regard to the free amines most probably carbamic acid chlorides, besides amine salt, are first formed, which latter reacts secondarily with phosgene, whereas the primary formed car-

bamid acid chloride is quickly subjected to the intermolecular reaction.

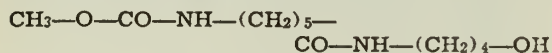
The product obtained according to the present invention may be used according to their properties in many different cases. Typically high molecular substances may be worked up according to the methods known for polyamides directly from the melt, from solutions or in a thermo-plastic process into fibers, ribbons, foils and similar structures. They may be furthermore formed into three-dimensional structures by spraying, dye-casting, pressing. Low polymeric materials for instance may be employed as starting materials for lacquer. Soft products may be used as substitute for wax. High polymeric and middle-high polymeric substances, relatively easy soluble in organic solvents, are adapted for auxiliary agents in the textile and leather industries and related branches of chemical technology, for instance for impregnations or fixations of pigments and dye-stuffs.

Example I

5-amino pentanol is transformed with chloroformic acid methyl ester into the carbamic acid methyl ester. This urethane is then heated in the presence of $1/200$ mol potassium carbonate at $140-200^{\circ}\text{C}$ until the separation of methanol ceases. The temperature is finally kept for 6 hours in vacuo (0.5 mm) at 210°C by simultaneously blowing dry, preheated nitrogen gas over the melt. The reaction product may be drawn into filaments directly from the melt.

Example II

N-carboxy methyl-amino capronic acid chloride obtained from the acid with thionyl chloride is caused to react in benzene solution with an aqueous solution of 1,4-amino-butanol in the presence of an alkali while cooling. The urethane thus obtained of the formula



is condensed with itself by splitting off methanol when heated, especially in the presence of catalysts adapted for the interchange of ester radicals, for instance $1/200$ mol toluene sulfo acid calculated on one mol urethane. The reaction may be carried out with and without solvents. A suitable solvent is o-dichlorobenzene.

Example III

Trans-4-amino-cyclo-hexanol is acylated in benzene with a calculated amount of chloroformic acid phenyl ester into urethane. The benzene is then distilled off and the product heated in the presence of traces of sodium phenolate in dry phenol at 170°C , until the viscosity does not increase any more. The reaction product is then precipitated as powder with acetone. It may be still further polymerized by remelting and reheating the melt in high vacuo.

A similar product is obtained, if the 4-amino-cyclo-hexanol is added to excess oxalic ester in alcohol and transformed into the oxamic acid ester which is heated in a nitrogen atmosphere in the presence of a little sodium alcoholate. The respective oxamic acid may be obtained also by saponification and then condensed.

Example IV

Finely powdered 1,4-butanol amine hydrochloride is suspended in chloro benzene. Therein is conducted phosgene at $100-130^{\circ}\text{C}$ under excess pressure of 60 mm Hg while violently stirring, until the development of hydrogen-chloride ceases. The mixture is then caused to boil while phosgene is permanently conducted through it, until hydrogen halide is no more detectable. Part of the diluent is finally distilled off. The reaction product is obtained in the form of a feebly colored powder, which may be still further polymerized by melting and further heating in vacuo.

PAUL SCHLACK.

ALIEN PROPERTY CUSTODIAN

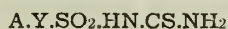
PROCESS FOR PREPARATION OF SULPHON-AMIDE DERIVATIVES

Zoltán Földi, Árpád Gerecs, István Demjén, and
Rezső König, Budapest, Hungary; vested in the
Alien Property Custodian

No Drawing. Application filed June 24, 1940

We have previously found that arylsulpho derivatives of 2-amino-thiazoles, in which the arylsulpho group contains an amino or a substituted or acylated amino group or other groups convertible into a group enumerated before, are either valuable therapeutics or valuable starting materials for preparing therapeutics. Such compounds are described in our U. S. Applications Ser. No. 267168 and Ser. No. 334990 respectively. Similar properties are shown by analogous thiazole derivatives in which the aryl group is replaced by a heterocyclic ring, such as by the pyridine ring.

According to present invention the above mentioned sulphonamide derivatives can be advantageously prepared by subjecting compounds of the general formula:



to the action of α -halogeno-ketones, -aldehydes, -acetals, -hemi-acetals, or of halogeno-acetals thereof, or of esters or ethers of the enolic forms, or of α -halogeno-carboxylic acids or of their esters. In the above standing formula A represents an amino, alkyl-amino, acylamino, or acylated alkylamino group, further other groups, such as nitro, azo, etc. groups, which are convertible into the different amino groups enumerated before; and Y represents an aryl or a heterocyclic group.

The present invention relates further to new 2-amino-thiazole-derivatives of anticoccic action, as well as new 2-amino-thiazole-derivatives, which are suitable starting materials to prepare new 2-amino-thiazole-derivatives of anticoccic action. Such new derivatives are e. g. 2-arylsulphamido-thiazoles, in which in the position 4 or 5 exo-alkyl-groups, such as aceto-, propio-, etc. groups are present or 2-arylsulphamido-thiazoles, in which the position 4 and 5 contain a bivalent aliphatic hydrocarbon chain of at least three carbon-atoms, or 2-arylsulphamido-thiazoles, in which the position 4 is substituted by a hydroxy-group or 2-arylsulphamido-thiazoles, in which the position 4 of the thiazole-ring is substituted by a hydroxy or alkoxy group and the position 5 is substituted by the carbalkoxy group. In all of these enumerated new compounds the arylsulpho-group contains in the para-position a member of the group, consisting of amino-, alkyl-amino-, acyl-amino-, acylated alkylamino-, nitro-groups.

Valuable starting materials are the acylamino-arylsulpho-thioureas, as well as the thioureides

of heterocyclic aminosulphonic acids, such as the acylamino-pyridine-sulphonyl-thiourea.

Arylsulphonyl derivatives of the thioureas have been unknown till yet, especially such arylsulphonyl-thioureas or thioureids of heterocyclic sulphonic acids, in which the aryl group or the heterocyclic nucleus contains amino or substituted or acylated amino groups, or other groups which are convertible into the groups enumerated before. The thiourea can not be, namely, acylated by acylating agents generally used for introduction of arylsulphonyl groups, because reactions of other course take place. Processes must have been created, thus, in order to obtain the starting materials of the present invention. These new starting materials can be obtained by splitting off α -alkoxy-alkyl group from the S-(α -alkoxy-alkyl)-ethers of the iso-thiourea acylated by an aromatic or heterocyclic sulphonic acid group. The starting materials for the latter process were as well unknown till yet. These starting materials can be obtained by subjecting iso-thiourea-ethers to the action of acylating agents suitable to introduce arylsulphonic groups or heterocyclic sulphonic acid groups. Such acylating agents are e. g. the arylsulpho halogenides, especially those, in which the aryl group is substituted by amino, alkylamino, acylamino groups or groups (such as nitro, azo, etc. groups) convertible into the groups mentioned before.

Such acylating agents are e. g. the acylamino-benzol-sulpho-halogenides, such as the p-acetyl-amino-benzosulphonyl chloride. Pyridine-sulphonyl halogenides can be used as well, e. g. the 2-acetamino-pyridine-5-sulphonyl bromide. One may use, preferably, as iso-thiourea-ethers the α -alkoxy-alkyl-ethers, such as the α -ethoxy-ethylether or, in the first place, the alkoxy-methyl-ethers, such as the methoxy-methyl or ethoxy-methyl ethers. These iso-thiourea-alkoxy-methyl ethers are preferably used in the form of their salts, as the free bases themselves are unstable. When using the salts, it is preferable to use acid binding agents, such as pyridine, sodium acetate, sodium alcoholate, etc.

Further details of the process for the obtention of arylsulpho-iso-thiourea-ethers are to be found in the examples.

The removal of the alkoxy-alkyl group from the aryl-sulpho-iso-thiourea ethers can be, preferably, effected by alcoholysis. For this splitting off specially those arylsulpho-iso-thiourea-alkyl ethers are suitable in which the alkyl group is an alkoxy-methyl or phenoxy-methyl group, preferably an ethoxy-methyl or methoxy-methyl group.

The alcoholysis is effected, preferably, in the presence of acid catalysts, such as dry hydrochloric acid. The alcoholysis is effected in an absolute alcohol, containing 0.1-0.3 percent of dry hydrochloric acid. As alcohol, the methyl- or ethyl-alcohol can be advantageously used. The alkoxy-methyl groups are split off by this alcoholysis in form of acetals of the formaldehyde. As starting materials for this hydrolysis acylamino-arylsulpho- or nitro-aryl-sulpho-iso-thiourea-alkoxy-methyl ethers can be preferably used.

Further details of the alcoholysis are to be found in the examples.

As other components for the process of the present invention α -halogeno ketones, such as α -chloro-acetone, 2-chloro-butanone-3 etc. can be used. Other valuable starting materials are further the α -halogeno derivatives of cyclic ketones or di-ketones or poly-ketones. Such compounds are for instance: α -chloro-cyclohexanone, the chloro- or bromo-acetylacetone symmetric, the bromo-di acetyl-monoxime. One may use preferably halogeno-ketones, as well, which contain further halogen-atoms, or oxy-, alkoxy, acyloxy groups as substituent. Such compounds are e.g. the di-chloro-acetone symmetric or the α -alkoxy, α' -chloro-acetones, etc. One may use further α -halogeno-aldehydes, such as chloro-acetaldehyde, α -bromo-propionaldehyde, etc. as well. Instead of the α -halogeno-ketones or -aldehydes one may use also their functional derivatives, such as acetals, hemi-acetals, ethers or esters of the enolic forms, etc. Such starting materials are e.g. the diaethyl-acetate of chlor-acetaldehyde, the 1,2-dichloroethylether, the chloro-ethylidene-diacetate etc. Valuable starting materials are further -halogenated oxo-carboxylic acids or their derivatives. Such compounds are e.g. the α -chloro- α -aceto-acetic acid ethyl-ester or the chloro-pyruvic acid or its esters, etc. One may further use α -halogenated acids or its esters or nitriles. One may use further α -halogenated derivatives of di- or poly-carboxylic acids or of their esters. Such compounds are e.g. the chloro-acetic acid, the chloroacetic acid ethylester, the bromo- or chloro-malonic acid diaethyl ester, the chloro-cyan-acetic-acid-ester, etc.

The reaction between the arylsulpho-thiourea and the α -halogenated oxo-compound is preferably carried out in the presence of an acid binding agent, such as of pyridine or other tertiary heterocyclic bases. The arylsulpho derivatives of the 2-amino-thiazole compounds result in this reaction generally in almost theoretical yield and in excellent purity, whereas the previous methods, in which the arylsulpho group is introduced into 2-amino-thiazole already preformed give generally mediocre yields. The present invention gives the possibility to obtain in a single operation amino-arylsulpho - 2 - amino - thiazoles, whereas the previous methods lead to acylamino-arylsulpho derivatives, which are to be subjected then to a deacylating treatment. Such a treatment however can be not always be effected, on account of the sensitiveness of many of the products in question.

Further details concerning the preparation of the starting materials and of the end-products are to be found in the examples.

1. Thiourea and chloro-methylether are brought into interaction in acetone at room-temperature. The hydrochloride of the iso-thiourea-chloro-methyl-ether separates. It melts at about 102°.

300 ccs of absolute methylalcohol are cooled to

-10° and 62.4 grams of chlorhydrate of iso-thiourea-methoxy-methylether are added. While stirring the hydro-chloride dissolves. Now a sodium-methylate solution is added in portion at -10°. The sodium-methylate solution has been prepared from 8.5 grams of sodium and 300 ccs of absolute methylalcohol. After the sodium-methylate solution has been added, 42 grams of finely powdered p-acetamino-benzolsulpho-chloride are added in portions at -10°, while stirring. The stirring is continued at -10°, then for about one hour at about 0°. The p-acetamino-benzolsulpho-iso-thiourea-methoxy - methylether separates as a crystal mass. It is now filtered, the precipitate washed with water in order to eliminate the sodium chloride, then dried. One obtains about 40 grams of a white crystalline product, which melts at about 167°. It can be recrystallised from alcohol.

One may prepare similarly the corresponding products, starting from benzolsulpho-chloride or from p-nitro-benzolsulpho-chloride or from 2-acetamino-pyridine-5-sulphonyl bromide.

2. 37.6 grams of finely powdered p-acetylaminobenzolsulpho-iso-thiourea-methoxy-methylether are boiled for a minute in 222 ccs of 93% methylalcohol and 1.1 ccs of absolute ethyl-alcohol, containing 33% hydrochloric acid gas. The starting material passes into solution and crystallisation occurs soon. The mixture is boiled for further 2 minutes, then allowed to cool, then cooled by ice-water. The crystals are filtered. One obtains 25-28 grams of p-acetylaminobenzolsulpho-thiourea, as a white crystalline powder, which melts at about 200.5°. It dissolves in diluted alcohol and can be reprecipitated without alteration by acidification with acetic acid.

The splitting off of the methoxy-methyl group can be effected also in ethylalcoholic medium. Instead of the methoxy-methyl-ether of the p-acetamino-benzolsulpho-iso-thiourea, one may use the ethoxymethylether or the α -ethoxy-ethylether as well. Instead of the p-acetamino-benzolsulpho-iso-thiourea ethers one may use the corresponding p-nitro-benzolsulpho-iso-thiourea ethers. One obtains, in this case, the p-nitrobenzol-sulpho-thiourea. From 2-acetaminopyridine-5-sulpho-iso-thiourea-methoxy - methyl-ether one obtains the 2-acetamino-pyridine-5-sulpho-thiourea.

3. 13.6 grams of p-acetyl-amino-benzolsulpho-thiourea, 14 grams of chloro-acetone and 340 ccs of alcohol of 80% are boiled for an hour, then evaporated in vacuo. The residue is ground with 30 ccs of dry acetone, the precipitate filtered and washed by 20 ccs of acetone. One obtains 9-10 grams of p-acetylaminobenzolsulpho-2-amino-4-methyl-thiazole, which melts without further purification at 252-257° under decomposition; it forms a white powder.

5 grams of this product are boiled with 50 ccs of 2-normal sodium hydroxide solution for half an hour and then cooled. The solution is then neutralised with acetic acid. 3.9 grams of p-amino-benzolsulpho-2-amino-4-methyl-thiazole separates, which forms, in this stage, a white powder and melts at about 237°, under decomposition.

4. 13.6 grams of p-acetamino-benzolsulpho-thiourea, 14 grams of chloracetone, 14 grams of pyridine and 200 ccs of alcohol of 80% are boiled for an hour on the water-bath. The reaction-mixture is evaporated in vacuo to dryness, the residue ground by water, filtered and dried. The p-acetamino-benzolsulpho-2-amino-4-methyl-

thiazole has been found in theoretic yield. It forms without further purification a white crystalline powder, which melts, under decomposition at about 257°.

5. 27.3 grams of p-acetamino-benzolsulphothiourea, 13.6 grams of chloroacetone, 20 ccs of pyridine are mixed. An exothermo reaction occurs, the materials passes temporarily, into solution. The mixture is then kept for 2 hours on the water-bath. On addition of 40-60 ccs of water the p-acetamino-benzolsulpho-2-amino-4-methyl-thiazole separates as white crystalline powder. The yield is theoretical.

6. 27.3 grams of p-acetamino-benzolsulphothiourea, 9.3 grams chloroacetone and 10 ccs of pyridine are mixed. An exothermo reaction and solution occurs, followed by an abundant precipitation of a crystal pulp. The mixture is kept for half an hour in the water-bath, then, after cooling, diluted with water and suctioned after standing. The p-acetamino-benzolsulpho-2-amino-4-methyl-thiazole is obtained in nearly theoretical yield as a white crystalline powder.

7. 8.6 grams of α,β -dichloro-diethyl-ether, 10 ccs of alcohol and 10 ccs of water are refluxed for half an hour in the boiling water-bath, then 13.6 grams of p-acetamino-benzolsulphothiourea and 22 ccs of pyridine are added. The mixture is kept for half an hour in the boiling water-bath, then evaporated to dryness, in vacuo. On addition of 100 ccs of water to the residue the p-acetamino-benzolsulpho-2-amino-thiazole crystallises out. The yield is about 90% of the theoretical. The product crystallises from aqueous alcohol in white crystals.

In the similar manner one may prepare by action of p-acetamino-benzolsulphothiourea on 3-chloro-butanone-2 the p-acetamino-benzolsulpho-2-amino-4,5-dimethyl-thiazole (melting point at about 264°), and the p-amino-benzolsulpho-2-amino-4,5-dimethyl-thiazole (melting point at about 248°), respectively; on 1-chloro-butanone-2 the p-acetamino-benzolsulpho-2-amino-4-ethyl-thiazole (melting point at about 218°) and the p-amino-benzolsulpho-2-amino-4-ethyl-thiazole (melting point at about 134°), respectively; on 1,1-dichloro-acetone the p-acetamino-benzolsulpho-2-amino-4-methyl-5-chloro-thiazole (melting point at about 217°) and the p-amino-benzolsulpho-2-amino-4-methyl-5-chloro-thiazole (melting point indefinite, at about 260°) respectively.

One may prepare likewise from 2-acetamino-pyridine-5-sulpho-thiourea with α -chloroacetaldehyde or chloroacetone the 2-acetamino-pyridine-5-sulpho-2-amino-thiazole or 4-methyl-thiazole respectively.

One may prepare further from p-nitro-benzolsulphothiourea and chloroacetone the p-nitro-benzolsulpho-2-amino-4-methyl-thiazole which crystallises from aqueous acetone in well developed yellow crystals, melting under decomposition at 200°. This product yields in an alcoholic suspension on hydrogenation, in the presence of palladium as catalyst, the p-amino-benzolsulpho-2-amino-4-methyl-thiazole.

8. 22 grams of p-acetylaminobenzolsulphothiourea, 14 grams of α -chloro-acetoacetic-ethyl ester and 22 ccs of dry pyridine are mixed. The temperature rises to 80°; in order to moderate the reaction the mixture is cooled with water. The pale yellow melted mixture is then kept for 10 minutes in the boiling water bath, then diluted by 400 ccs of water. The oil, which precipitates crystallises quickly. It is suctioned and washed

with water. One obtains the ethyl-ester of 2-(p-acetylaminobenzolsulphamido)-4-methyl-thiazole-5-carboxylic acid in theoretical yield. It melts at 247-49°. The product can be recrystallised from large amounts of hot alcohol.

On saponification by means of diluted sodium hydroxide the acetyl group is split off and the carbethoxy group, as well, is saponified. 1 gram of the above described product is boiled in 10 ccs of sodium hydroxide of 10 volume % for half an hour, then acidified, to litmus, by about 2 ccs of conc. hydrochloric acid. White crystalline powder separates, which is suctioned and washed by water. One obtains 0.75 grams of 2-(p-amino-benzolsulphamido)-4-methyl-thiazole-5-carboxylic acid, which can be recrystallised from about the thirtyfold amount of methylalcohol. The product shows two melting points, the first being at about 176-183°, while the second melting occurs at about 237°. If only the acetyl group is wanted to be split off, while the carbethoxy group is wanted to be left unaltered, one may proceed as follows: 4 grams of 2-(p-acetylaminobenzolsulphamido)-4-methyl-5-carbethoxy-thiazole are boiled in 20 ccs of absolute alcohol containing about 1.6 grams of hydrochloric acid gas. After boiling for about 8-10 minutes a white crystalline mass separates. After having been boiled for an hour, the reaction mixture is cooled, the crystals suctioned and washed by cold alcohol. One obtains in nearly theoretical amount the hydrochloride of the 2-(p-amino-benzolsulphamido)-4-methyl-5-carbethoxy-thiazole, which melts under decomposition, at 230-231°. One may obtain the free base in likewise theoretical yield by treating the hydrochloride with sodium acetate solution. The product can be recrystallised from about the sixfold amount of boiling alcohol and melts at about 196°. It shows an excellent anticoccic action.

9. 1.15 grams of p-amino-benzolsulphothiourea, 0.85 grams of α -chloro-acetoacetic acid ethylester and 2 ccs. of pyridine are mixed. Dissolution and elevation of temperature occurs. The mixture is kept for a quarter of an hour in the boiling water-bath, then 20 ccs. of water are added. On longer standing crystals separate, which are suctioned and washed by water. One obtains in nearly theoretical amount the 2-(p-amino-benzolsulphamido)-4-methyl-5-carbethoxy-thiazole, which melts, thus prepared, at 130-134° and is probably an isomer of the corresponding product described in example 8. A sample of the product melting at 130-134°, dissolved in sodium hydroxide and reprecipitated by acidification with acetic acid, gives a product, which melts at more than 30° higher temperature than originally.

When using in the above standing two examples instead of the ethylester the methyl-, butyl-, amyl-, or benzyl-, etc. esters of the chloro-acetoacetic acid, one obtains the corresponding thiazole derivatives, in which the carboxylic group in the position 5 is esterified by the corresponding alcohols.

When starting from the α -chloro-acetoacetic diethyl-amide, one obtains the thiazole derivative, in which the position 5 is substituted by the diethyl-carboxyl amide group.

When using the p-nitro-benzolsulphothiourea, one obtains the p-nitro-benzolsulpho-2-amino-4-methyl-thiazole-5-carboxylic acid derivatives.

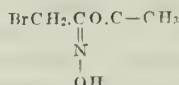
10. 2.7 grams of mono-chloro-acetylacetone symmetric, 5.5 grams of p-acetylaminobenzolsulphothiourea and 6 ccs of dry pyridine are

mixed. A violent reaction takes place. The pale yellow melted mixture solidifies in crystals, on standing. After addition of 40 ccs of water it is ground and suctioned and washed by water. One obtains, in theoretical amount, the 2-(p-acet-
amino-benzolsulphamido)-4-methyl-5-aceto-thi-
azole, which does not melt till 280°.

2.5 grams of this product are boiled in 20 ccs of sodium hydroxide of 10 volume % and in 5 ccs of water. The pale yellow solution is acidified by 2.5 ccs of glacial acetic acid. The precipitate is filtered, washed by water and dried. The product is boiled with 9 ccs of absolute alcohol, then cooled and filtered. One obtains the 2-(p-amino-benzolsulphamido)-4-methyl-5-aceto-
thiazole, which melts at 213-14°.

The same product can be obtained by condensing mono-chloro-acetylacetone with p-amino-benzolsulpho-thiourea.

11. 3.6 grams of the mono-bromo-diacetyl-monoxime according to the formula:



and 5.5 grams of p-acetamino-benzolsulpho-thiourea and 6 ccs of dry pyridine are mixed. Under elevation of temperature a yellowish melt is formed, which is kept some minutes on the water-bath, then cooled and added by 20 ccs of water. On cooling and standing white crystals separate, which are suctioned and washed by water. One obtains the 2-(p-acetyl-amino-benzolsulphamido)-4-aceto-thiazole-oxime, which melts at about 204°. It dissolves readily in 1/2-normal sodium hydroxide.

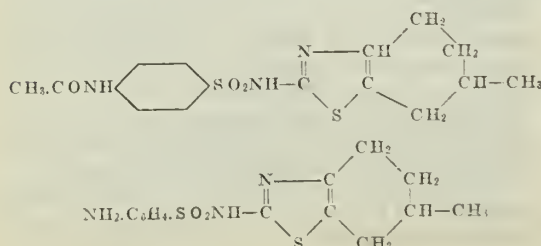
On splitting off the acetyl group as well as the hydroxylamine by hydrolysis, one obtains the corresponding 4-aceto-derivative.

12. 132 grams of α -chloro-cyclohexanon, 273 grams of p-acetamino-benzolsulpho-thiourea and 300 ccs. of dry pyridine are stirred and warmed on the water-bath. The reaction components go into solution. Then the mixture is cooled and the thick syrup is mixed with 2 litres of water. An oil separates, which crystallises soon. After standing the crystals are filtered, washed and dried. For further purification they can be crystallised from large amounts of hot alcohol of 90%. One obtains the 4,5-tetramethylene-2-(p-acetyl-amino-benzolsulphamido)-thiazole, which melts at about 265-280°.

This product, boiled with the eightfold amount of sodium hydroxide of 10 volume % for half an hour and then acidified by hydrochloric acid, yields the 4,5-tetramethyl-2-(p-amino-benzolsulphamido)-thiazole, melting at about 244°. The product has anticoccic action.

When using, instead of p-acetylaminobenzolsulpho-thiourea, the p-amino-benzolsulpho-thiourea, one obtains directly the product described above.

One may obtain similarly from 2-chloro-methyl-cyclo-hexanone the compounds of the formula:



Starting from the cyclic α -halogeno-ketones mentioned in this example and condensing them with p-nitro-benzolsulpho-thiourea or with benzolsulpho-thiourea, one obtains the corresponding nitrobenzolsulphonyl- or benzolsulphonyl-amino-thiazole derivatives.

13. 7.5 grams of ethyl chloro-acetate, 16.5 grams of p-acetamino-benzolsulpho-thiourea and 13 ccs of pyridine are mixed. The temperature rises to about 40° and a dissolution occurs. After heating on the waterbath for about a quarter of an hour, the mixture is diluted by 150 ccs of water, upon which the p-acetyl-amino-benzolsulpho-2-amino-4-oxy-thiazole separates as a crystalline powder. The yield is about 75% of the theory. It decomposes at 258-59°.

14. 12.5 grams of ethyl chloro-acetate, 23 grams of p-amino-benzolsulpho-thiourea and 30 ccs of pyridine are mixed. A slight elevation of the temperature takes place and the materials go into solution. The mixture is then heated on water-bath for half an hour, then diluted by 150 ccs of warm water. On cooling the p-amino-benzolsulpho-2-amino-4-thiazole crystallises in compact crystals, melting at 235-37°. The yield is about 60% of the theory.

15. 4 grams of chloro-malonic diethyl ester, 5.5 grams of p-acetamino-benzolsulpho-thiourea and 6 ccs of pyridine are mixed, then heated at about 60° for a quarter of an hour. One obtains a homogeneous yellow syrup, which solidifies after standing for 2 hours. On addition of 70 ccs of water, the crystals dissolve, followed soon by precipitation of white crystals. One obtains 7.05 grams of crystals, melting at 164° under development of gas. The product is recrystallisable from alcohol, the melting point rising thus to 165-166°. The product is the 4-oxy- or 4-ethoxy derivative of p-acetamino-benzolsulpho-2-amino-5-carbomethoxy-thiazole.

16. 4.8 grams of bromo-malonic diethylester, 4.6 grams of p-amino-benzolsulpho-thiourea and 6 ccs of pyridine are mixed upon which the temperature rises to about 75°. The yellow thick syrup thus formed, is heated on the water-bath for 10 minutes, then allowed to stand for an hour and a half, and then diluted by 80 ccs of water. The homogeneous solution deposits 5.9 grams of pale yellow crystals, which melt between 136-138°. This product recrystallised from alcohol, melts at 138-139°, under decomposition. The product is the deacetylated derivative of the product described in the preceding example.

17. 62 grams of p-acetamino-benzolsulpho-thiourea, 35 grams dichloro-acetone symmetric and 17-18 grams of pyridine are heated in 100 ccs of alcohol of 80% on the water-bath. One obtains a solution which is boiled for further 10 minutes, then poured into 450 ccs of ice-water. The crystals separated on longer standing are collected and washed with water. They are dried in vacuo. One obtains about 71 grams of p-acetamino-benzolsulpho-2-amino-4-chloromethyl-thiazole, which melts at about 203°, under decomposition.

When using p-amino-benzolsulpho-thiourea instead of p-acetyl-amino-benzolsulpho-thiourea, one obtains the p-amino-benzolsulpho-2-amino-4-chloromethyl-thiazole.

10 grams of p-acetamino-benzolsulpho-2-amino-4-chloromethyl-thiazole are boiled on water-bath in 100 ccs of absolute alcohol containing about 10% of hydrochloric acid gas. After about half an hour a complete dissolution takes place, followed soon by crystallisation. The mix-

ture is boiled further for 10 minutes, then cooled, the crystals are collected, washed by absolute alcohol and dried in vacuo. One obtains the hydrochloride of the p-amino-benzol-sulpho-2-amino-4-chloromethyl-thiazole, which does not melt till 290°.

3 grams of this hydrochloride are shaken with 50 ccs of acetic ether and 20 ccs of sodium acetate solution of 10%. After dissolution has been observed, the acetic ether layer is separated, dried upon sodium sulphate and evaporated in vacuo. The residue is crystallised from glacial acetic acid.

One obtains the p-amino-benzosulpho-2-amino-4-chloromethyl-thiazole, melting at 120°. As the chloro-atom is very reactive, it is advisable to make the above described operations at low temperature and without loss of time, in order to restrict the hydrolysing effect of the water.

5 grams of p-acetamino-benzosulpho-2-amino-4-chloromethyl-thiazole are boiled with 50 ccs of hydrochloric acid of 10% for half an hour, then the acidity partially neutralised by ammonia. Impurities separate, which are filtered and the filtrate treated by animal charcoal. The filtered solution is now completely neutralised by ammonia. On cooling the p-amino-benzosulpho-2-amino-4-oxymethyl-thiazole crystallises; it melts at about 201°.

When condensing α -metho- α' -chloro-acetone with p-amino-benzosulpho-thiourea, one obtains the methyl-ether of the above-described product. When condensing p-acetamino-benzosulpho-thiourea with 4-amino- or 4-acetamino- α -chloro-acetophenone, one obtains the p-acetamino-benzosulpho-2-amino-4-(p'-amino-phenyl)-thiazole—melting point at 173–175°, or the 4-(p'-acetamino-phenyl)-thiazole—melting point at 280–281°—respectively.

By condensing p-amino-benzosulpho-thiourea with 4-amino- or 4-acetamino- α -chloro-acetophenone, one obtains the p-amino-benzosulpho-2-amino-(p'-amino-phenyl)-thiazole—melting point at 102–103°—or the -(p'-acetamino-phenyl)-thiazole—melting point at 275–77°—respectively. By condensing p-amino-benzosulpho-thiourea with 4-chloroacetopyrocatechine, one obtains the p-amino-benzosulpho-2-amino-4-(3',4'-dioxo-phenyl)-thiazole.

The experimental conditions given in the examples can be varied in many other respects as well.

ZOLTÁN FÖLDI.
ÁRPÁD GERECS.
ISTVÁN DEMJÉN.
REZSÖ KÖNIG.



ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF SOLUTIONS OF CELLULOSE IN SULFURIC ACID

Heinrich Fink and Richard Hofstadt, Rottweil
A. N., Germany; vested in the Alien Property
Custodian

No Drawing. Application filed July 10, 1940

This invention relates to the manufacture of solutions of cellulose in sulfuric acid.

It is known to dissolve cellulose in mineralic acids, such as sulfuric acid, phosphoric acid, hydrochloric acid and other acids or mixtures thereof, and to work up these solutions into fibers, films or similar structures of this kind. In this case the cellulose is first thoroughly swollen with a weaker acid near the dissolving concentration and finally completely dissolved with an acid of higher concentration.

Furthermore it is known that cellulose in these strongly acid solutions is easily decomposed, and that the production and working up of these solutions is therefore connected with considerable difficulties.

It is an object of the present invention to provide a method of dissolving cellulose in sulfuric acid, which is free from these disadvantages.

This and other objects will become apparent from the following specification.

The present invention relates to the manufacture of solutions of cellulose in strong sulfuric acid, whereby the cellulose is first impregnated or wetted with a weaker acid (wetting acid) and then dissolved in a strong acid (dissolving acid).

The process comprises impregnating the cellulose with only $2\frac{1}{2}$ –3 times its weight of wetting acid and adding so much of dissolving acid of a concentration above 90%, that the total amount of sulfuric acid used for complete solution (calculated as monohydrate) amounts to not more than 5 times, preferably 4 times and less, the weight of cellulose.

It has always been endeavoured in the art to dissolve in the strong acids as much cellulose as possible, but in spite of this in no case there were reached concentrations higher than 1 kg. cellulose in 8 liters strong acid, as the concentrations of the acids applied and the working methods did not admit the dissolution of larger quantities of cellulose.

When wetting the cellulose with an amount of acid just being sufficient, it is difficult to impregnate evenly the entire cellulose. When working too slowly and when using a swelling acid, the latter being near the dissolving concentration, part of the cellulose takes up the total amount of sulfuric acid, whereas the other part remains dry. Also when mixing and kneading continuously such an uneven cellulose-sulfuric-acid-mixture, an even distribution of the sulfuric acid in the cellulose mass can never be obtained. On the other hand it is impractical to use the wetting acid in too weak a concentration, since solutions of high cellulose contents are required, for which then correspondingly higher amounts of dissolving acid are necessary. Most suitable for that purposes are concentrations between 55–59% H_2SO_4 .

Though it is possible when working quickly and with not too large quantities, to evenly impregnate the cellulose being suitably distributed with 2.5–3 times its quantity of 55–59% acid, if said acid is added to the mass all at once while stirring violently, it is generally to be preferred to employ a larger surplus of wetting acid and to squeeze it off again as quickly as possible. When squeezing off the acid, care has to be taken, that the cellulose, though completely impregnated, has not yet reached the maximum degree of swelling, which may be brought about by adapting the concentration of the wetting acid to the swelling capacity of the employed cellulose material. The right concentration is easily determined in every case by some pretests. The right degree of pressing the cellulose can be, for instance, brought about by impregnating the cellulose breadth with wetting acid of the right concentration on a continuous belt conveyer and immediately squeezing off the acid between press rolls.

While hitherto 10 times the weight of wetting acid has been used for the impregnation of the cellulose, it may be attained, when working properly and adjusting properly the concentration to the kind of cellulose material, that the weight of the cellulose pulp amounts to only 3 times, sometimes 2.5 times that of the cellulose.

In order to cause dissolution of the cellulose, it is necessary to employ an extremely high concentration of the dissolving acid which hitherto was unusual, for instance 90–96% H_2SO_4 . Also sulfuric acid monohydrate may be employed, while cooling, without causing a harmful decomposition of the cellulose. The amount of the dissolving acid required depends on the concentration. Solutions containing 4–5 parts H_2SO_4 (monohydrate) for one part cellulose are relatively easy obtained, provided the concentration of the acids was properly chosen and the mass properly cooled. The high cellulose contents of the solutions are quite useful for the manufacture of filaments and films, when working up the solutions, because large quantities of sulfuric acid and precipitating agents can be safed in this way. Especially useful is also, that these solutions are relatively stable.

It is evident that the cellulose solutions according to the present invention are so extremely viscous, that the viscosity cannot be determined any more according to known methods. The spinning of the solutions, however, with known devices, for instance by using spinning nozzles of an inner width of 0.09 mm, is easily feasible. An increased pressure, however, has to be applied to extrude the solutions through the nozzles. 50–60 atmospheres are completely sufficient in most cases.

Example I

475 grams cellulose (air dry) are brought together at 0° in a mixing vessel with 1500 grams sulfuric acid of 95% H_2SO_4 and are then homogenized in a suitable device adapted for kneading, while cooling continuously. There are added to the cellulose pulp 1060 grams sulfuric acid of 96% H_2SO_4 , which are also very well pre-cooled. After a short time there is obtained a clear solution which can be spun or worked up in a manner known per se into filaments, films and the like; it contains

	Percent
Cellulose -----	14.7
H_2SO_4 -----	62.7
Water -----	22.6

Example II

Cellulose (air dry) is impregnated at 0° in the form of plates or directly from the continuous belt conveyer in sulfuric acid of 59% H_2SO_4 in such a way, that always 400 grams cellulose are

brought together with 3000 grams sulfuric acid of 59% and squeezed down to 1000 grams in the usual way by means of cell filters or pressrolls. The cellulose thus treated is brought together, while continuously cooling, after it has been loosened up in a mixing vessel adapted for kneading or otherwise suitable with 1080 grams sulfuric acid of 91% H_2SO_4 , whereby the sulfuric acid must be pre-cooled very well. After a short time a solution is obtained, which may be worked up according to Example I.

Example III

550 grams cellulose (air dry) are impregnated at 0° with 3000 grams sulfuric acid of 59% and shortly afterwards squeezed down to 1550 grams. This mass is homogenized, while cooling, in a crusher or kneading device and thereto are added 250 grams oleum of 25% SO_3 . A pasty clear solution, in which the sulfuric acid amounts to less than double the amount of cellulose, is obtained.

HEINRICH FINK.

RICHARD HOFSTADT.

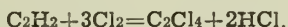
ALIEN PROPERTY CUSTODIAN

PROCESS OF MANUFACTURING TETRACHLOROETHYLENE

Hans Werner Schmidt, Berlin, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed July 12, 1940

My invention relates to improvements in the process of manufacturing tetrachloroethylene C_2Cl_4 from ethane tetrachloride. Processes in which ethane tetrachloride or ethylene trichloride in mixture with the corresponding amount of chlorine at elevated temperature are passed in contact with the catalysts, such as active carbon, are known. In these processes tetrachloroethylene is produced while hydrogen chloride is split off. The reaction follows the following equation



Accordingly in the known processes for 1 mol of acetylene 3 mols of chlorine are needed, 2 mols of chlorine being consumed for producing the tetrachloroethylene, while 1 mol is transformed, in one of the said known processes, into chloride of an alkaline earth or an alkali metal, or, in a more recent catalytical process, into hydrogen chloride.

One of the objects of the invention is to provide a process by means of which tetrachloroethylene can be obtained in a more simple and less expensive way. Another object of the invention is to provide a process which is more economical with reference to the consumption of chlorine and in which more particularly the amount of chlorine needed for transforming ethane tetrachloride into tetrachloroethylene is materially reduced. Another object of the invention is to provide a process in which the total amount of chlorine entered into the process is made use of for forming tetrachloroethylene. Other objects of the invention will appear from the following description describing an embodiment of the invention in detail.

I have discovered that tetrachloroethylene C_2Cl_4 can be manufactured with only 2 mols of chlorine per mol of acetylene if the ethane tetrachloride in the form of vapor and in the presence of oxygen or gaseous mixtures containing oxygen is passed at elevated temperature over catalysts causing the oxidation of hydrogen chloride to chlorine. The hydrogen chloride which is at first produced by the thermic reaction is oxidized by the oxygen into elementary chlorine, and the said chlorine is immediately consumed for forming tetrachloroethylene. The process may be represented in a general way by the following equations:

- (1) $2C_2H_2Cl_4 - 2C_2HCl_3 + 2HCl$
- (2) $2HCl + \frac{1}{2}O_2 = Cl_2 + H_2O$
- (3) $C_2HCl_3 + Cl_2 = C_2HCl_5$
- (4) $C_2HCl_5 - C_2Cl_4 + HCl$
- (5) same as 2, etc.

As catalysts any substances or mixtures of substances may be used which are suitable for oxidizing hydrogen chloride, for example copper compounds such as copper oxide, copper chloride (preferably cuprichloride) or copper sulphate, further, the corresponding compounds of iron, chromium, manganese, and cerium, which compounds may be used either separately or in mixture, further, all the aforesaid substances, either separately or in mixture, together with aluminum oxide, magnesium oxide, bismuth oxide etc. Preferably the said substances are applied to suitable carrier substances, such as clay, pumice, gypsum, silicic acid gel, alumina gel, and the like.

As in any other case, the velocity of the flow of the gases depends on the volume of the catalyst.

The longer the path of the gases through a catalyst, the higher may be the velocity of the flow thereof. The flow velocities and the temperatures are not at a definite ratio directly depending from one another, the formation of tetrachloroethylene being bound to definite temperature limits, as in any other catalytical process.

The process may be carried out at temperatures of from 300 to 500° C. and preferably at temperatures of from 370 to 450° C.

The amount of the ethane tetrachloride exposed to the action of the catalyst may be as high as from 100 to 150 grams ethane tetrachloride per hour and per liter of the catalyst, the filling consisting of clay in pieces of from 2 to 4 millimeters in diameter coated with from 5 to 10% copper chloride. In each case the said amount depends on the amount and the character of the catalyst per unity of volume.

A suitable material from which the reaction pipe may be made, is for example, ceramic material or other material resistant to hydrogen chloride and chlorine.

The formation of tetrachloroethylene begins also if the amount of oxygen is stoichiometrically insufficient. But it rises as the amount of oxygen is increased. Preferably the reaction is carried out with an excess of oxygen exceeding the stoichiometric ratio, for example, with an excess of from 20 to 80%, because in this case the product of the reaction contains much tetrachloroethylene. At a temperature of from about 400 to 430° and an excess of oxygen of more than 20% with a copper chloride-clay catalyst a reaction product was obtained which contained 90% and more of tetrachloroethylene.

The oxygen may be used in concentrated form or diluted with inert gases, for example, air.

The reaction products are collected while cooling in water, the hydrochloric acid which is present in comparatively small amounts being dissolved. The chlorinated products are precipitated, and after separation from the watery phase, they are separated from one another by fractionated distillation. This is the most simple method of separating the components though other separating methods may be used which are known in the art.

As compared to known processes my improved process is preferable because practically the whole amount of the chlorine entered into the process is made use of for producing tetrachloroethylene, while in known processes one third of the chlorine is transformed into chlorides of alkali or alkaline earth metals, which have no value whatever or into hydrogen chloride, the value of which is less than that of the tetrachloroethylene.

Example

Ethane tetrachloride vapor and a corresponding amount of air ascertained by calculation were passed at a temperature of from 430 to 450° C through a pipe containing pieces of pumice impregnated with cupri-chloride. The flow velocity of the gaseous mixture was about 120 grams of ethane tetrachloride per hour and per 800 cubic-centimeters of catalyst volume. In addition to some ethylene trichloride, ethane pentachloride and watery hydrochloric acid the product of the reaction substantially consisted of tetrachloroethylene.

While in describing the invention reference has been made to a particular example embodying the same I wish it to be understood that my invention is not limited to the specific process described herein, and that various changes may be made such as will readily suggest themselves to those skilled in the art.

HANS WERNER SCHMIDT.

ALIEN PROPERTY CUSTODIAN

METHOD OF MANUFACTURING AZO COM-
POUND OF CINCHONA ALKALOIDTakeo Takayanagi, Tomokomai-Machi, Yufutsu-
Gun, Hokkaido, Japan; vested in the Alien
Property Custodian

No Drawing. Application filed July 18, 1940

The present invention relates to a method of manufacturing anti-bacterial azo compound, which comprises diazotising monocyclic or polycyclic aromatic amine or heterocyclic amine and causing the same to act upon a substance retaining the hydroxyl group of phenol in the quinoline residue of cinchona alkaloid. The object thereof is to obtain new anti-bacterial azo compound of cinchona alkaloid. There has been already proposed a method of manufacturing azo compound which shows anti-bacterial action. Now, according to this invention it has been found that if monocyclic or polycyclic aromatic amine or heterocyclic amine is diazotized in the usual manner and is caused to act upon a substance having the hydroxyl group of phenol in the quinoline nucleus of cinchona alkaloid, it is possible to obtain new antibacterial azo compound. This invention is based on such insight and is characterised by the fact that in the manufacture of anti-bacterial azo compound monocyclic or polycyclic aromatic amine or heterocyclic amine is diazotized and is made to act upon a substance retaining the hydroxyl group of phenol in quinoline residue of cinchona alkaloid. In this case, the cyclic amine to be diazotized for the object of this invention may be to the compounds described in the following two categories:

I. Carbocyclic compounds.

(a) Monocyclic aromatic compounds.

(1) Aromatic amines.

Toluidine, xylidine, phenylene-diamine, amino N-alkylated aniline, amino N-acylated aniline and aniline substitution product.

(2) Amino azo compounds.

Amino azo benzol, amino azo toluene, diamino azo benzol, diamino azoxy benzol, amino azo benzol sulphonic acid, benzol disazo benzol aniline, amino azo benzol-4'-sulphone amide, amino azo benzol-4'-arsenic acid and amino azo benzol-4'-stibinic acid.

(3) Amino phenols.

Amino phenol, amino phenol alkyl ether and amino resorsine.

(4) Amino benzol sulphonic acid, its sulphonamide and a compound with the hydrogen of the amino group of this sulphonamide substituted by the following atomic groups or a compound with the amino group substituted by cyclic aromatic amine:—

Amino benzol sulphonic acid, amino benzol sulphonamide, amino benzol sulphonacylamide, amino benzol sulphonalkylamide, amino benzol sulphonamide benzol sulphonamide, amino benzol sulphonpyridine amide, amino benzol sulphonazo benzol amide and amino benzol sulphonanilide.

(5) Aromatic carboxylic acid having amino group, its carboxylic acid amide, a compound with the hydrogen of the amide group of this carboxylic acid amide substituted by the following atomic groups or a compound with the amino group substituted by cyclic amine, namely:—

Amino benzoic acid, amino benzoic acid alkyl, anthra-nilinic acid, amino salicylic acid, amino salicylic acid alkyl ester, amino cinnamic acid, amino benzoic acid amide, amino benzoic acid acyl amide, amino benzoic acid alkyl amide, amino benzoic acid diethyl amide and amino benzoic acid pyridine amide.

(6) Aromatic amines having a metal-containing atomic group as a substituted group.

Amino phenyl arsenic acid, amino phenyl oxyarsenic acid, amino phenyl stibinic acid, amino oxyphenyl stibinic acid, amino oxyphenyl arsenic oxide, amino phenyl arsenic oxide, amino thiophenyl, amino oxyphenyl stibine oxide, amino phenyl arsen chlor stibinine, amino phenyl arsen chlor bismuth and amino arsen phenyl stibinic acid.

b. Polycyclic aromatic amines.

(1) Amino diphenyls.

Benzidine, dianisidine, benzidine sulphone, diamino azo diphenyl, diamino diphenyl methane, diamino stilbene, diamino diphenyl amine and diamino carbazol.

(2) Amino naphthalenes.

Naphthyl amine, naphthylene diamine, amino naphthol and amino naphthol sulphonic acid.

(3) Amino anthracenes.

(4) Amino phenanthrenes.

II. Heterocyclic compounds.

(1) Amino pyridines.

(2) Amino quinolines.

(3) Amino pirazolones.

Amino antipyrine.

(4) Amino iso quinolines.

(5) Amino acridines.

3-6-diamino, 10-methyl acridinium chloride and 2-ethoxy 6-9-diamino acridine.

The other nucleus bound to azo bridge, viz. cinchona alkaloid must retain free hydroxyl group in its quinoline nucleus like the natural cupreine. But in the general cinchona alkaloid said hydroxyl group being present as alkyl ether, it is saponified with mineral acid, alkali, or a halogen-supplying substance by heating and after thus liberating the hydroxyl group, is acted upon by the above-mentioned cyclic diazo compound.

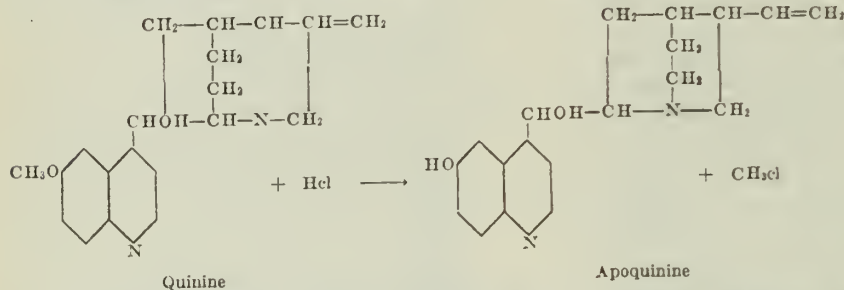
For instance, cupreine is bound directly to diazonium and forms azo dyes. Quinine has no such property. But if it is demethylated, apoquinine is produced, while if hydroquinin is demethylated, hydrocupreine is produced. If this is bound to the above cyclic diazonium compound,

azo dye is formed quantitatively. The natural cupreine is applicable to the object of this invention as such, but the under-mentioned cinchona alkaloid and its derivatives may be used for the object of this invention after they are saponified and de-alkylated to retain free hydroxyl group:

Quinine, quinidine, quinotoxin, quinone, iso-quinine or a compound obtained by dihydrating, hydrohalogenating, dihalogenating or hydroxylating the vinyl group of the above cinchona alkaloid, a compound with the alcoholic hydroxyl of the above cinchona alkaloid substituted by halogen or a compound obtained by halogenating the quinoline nucleus of the above cinchona alkaloid.

To saponify and de-alkylate cinchona alkaloid and its derivatives, they are saponified by heating directly or in a suitable solvent with mineral acids such as fuming hydrochloric acid, nitric acid, sulphuric acid, hydrobromic acid, etc. or halogen supplying substances such as aluminium chloride, sublimated chloride of iron, tin tetrachloride, antimony pentachloride, phosphorous oxychloride or caustic alkali.

The reaction in this case takes place according to the following formula:



If, when the quinoline residue of cinchona alkaloid has the hydroxyl group of phenol as stated before, the before-mentioned cyclic compound having amino group is bound to it systematically by diazo band in the usual manner as enumerated below, there is obtained the new azo compounds of cinchona alkaloid which show various anti-bacterial actions.

To bind cyclic diazo compound to cinchona alkaloid having hydroxyl group, alkaline reaction is necessary, and the reaction is most satisfactory where the solution becomes weak alkaline or neutral after the completion of the reaction. Further, the temperature of the solution at the time of combination is properly 0° C. or below 5° C. The yield is good in all the cases and is quite quantitative.

The product of the present invention is specially effective against warm blooded animals' (man or animal) pneumonia, suppurative diseases, diseases relating to cold, the diseases caused by spirovorn, gonococcus diseases and other diseases for which quinine is good.

It is known that quinine has a special virtue for protozoally and bacterially caused diseases. This pharmacological action is said to be done by the quinoline nucleus of quinine as the root and the three accessory side chains, namely, methoxyl, vinyl and hydroxyl groups. What is interesting is that it is publicly known to prepare a remedy for pneumonia by merely substituting ethoxyl for the methoxyl of quinine. Also, the change of these three side chains and chemical treatment have been studied deeply.

According to the present invention, a new deparature has been made in chemical treatment by

introducing various kinds of cyclic amines into the quinoline nucleus of cinchona alkaloid with a new side chain (fourth side chain), diazo bridge N.N, in addition to be known three ones.

The products of this invention are azo dyes of orange deep red, reddish purple and dark green colors and have a bitter taste. They generally have the property of cinchona alkaloid and are hard to dissolve in water, but easily dissoluble in alcohol and other organic solvents. By combining with acids, they form a salt soluble in water fairly well. They generally produce insoluble precipitates by alkaloid reagent.

The following are examples of the manner of manufacturing the new azo compound of cinchona alkaloid by binding cyclic amine systematically to cinchona alkaloid having hydroxyl group according to the classification already described:

Example I

Obtaining anti-bacterial azo compound by causing the diazo compound of aromatic amines to act upon the before-mentioned cinchona alkaloid group.

(1) 10 grams of para-toluidine is dissolved in 30 cubic litres of hydrochloric acid and 100 cubic centimeters of water and the solution is diazotized by 7 grams of sodium nitrite. If it is added to 32 grams of hydro cupreine, 20 grams of caustic soda and 400 litres of water with the addition of ammonia, red crystals of the melting point of 148° C. are obtained, while if para nitro aniline is diazotized and bound to apoquinine, crystals of vermilion color of the melting point of 118° C. are produced.

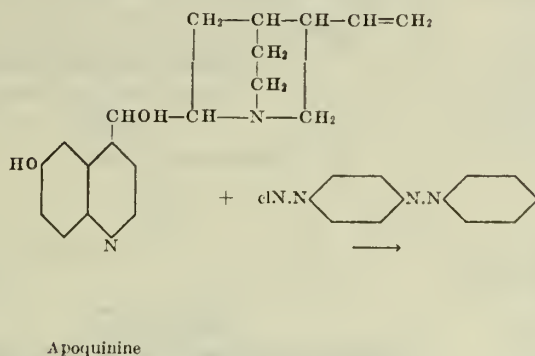
(2) 14 grams of para amino dimethyl aniline is dissolved in 50 cubic centimeters of concentrated hydrochloric acid and the solution is diazotized by 7 grams of sodium nitrite. Then, it is added to a mixed solution of 32 grams of apoquinine, 35 grams of caustic soda and 500 cubic centimeters of water. From the thus-obtained solution of purple grey color, crystals of the melting point of 156° C. are obtained by ammonia.

(3) By similarly diazotising 13 grams of ortho chlor aniline and causing it to act upon 32 grams of apoquinine, crystals of orange color of the melting point of 85° C. are obtained.

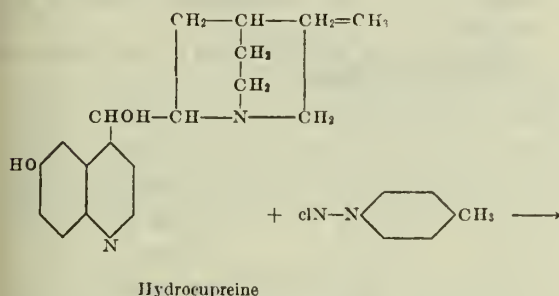
(4) By diazotising 15 grams of para amino acethanilide in the similar manner and making it act upon 32 grams of apoquinine, red azo compound is obtained.

(5) After adding 15 grams of sodium nitrite to 80 cubic centimeters of concentrated hydrochloric acid and 400 grams of pieces of ice while cooling the latter with a cooling agent, a solution obtained by dissolving 11 grams of paraphenylene diamine in 15 cubic centimeters of concentrated hydrochloric acid and 10 cubic centimeters of water is added. Next, this solution is added to a

mixed solution of 64 grams of hydrocupreine, 60 grams of caustic soda and 400 cubic centimeters of water, and from the thus-obtained dark purple color solution crystals are produced by ammonia.



The following is the formula of the typical reaction in this example:



Example II

If amino azo compound is diazotised and is made to act upon the abovementioned cinchona alkaloid group, an anti-bacterial dye of the property capable of dyeing fat is obtained.

(1) 20 grams of paraamino benzol is dissolved in 50 cubic centimeters of concentrated hydrochloric acid and 400 cubic centimeters of water, and after diazotising the solution by 7 grams of sodium nitrite, it is added to 32 grams of apoquinine, 35 grams of caustic soda and 400 cubic centimeters of water and bound to them after the completion of the reaction, it is acidified by hydrochloric acid and crystals of bloody red color of the melting point of 145° C. are obtained from it by ammonia. In the similar way, crystals of deep red color are obtained from hydrocupreine. If paraamino azo toluol is diazotised in the usual manner and bound to apoquinine, red crystals of the melting point of 128° C. are obtained.

(2) By diazotising orth amino azo toluol and binding it to apoquinine, crystals of carmine red color of the melting point of 160° C. are produced.

(3) Similarly, if amino azo benzol sulphon amide is diazotized and bound to apoquinine, crystals of dark red color of the melting point of 165° C. are obtained.

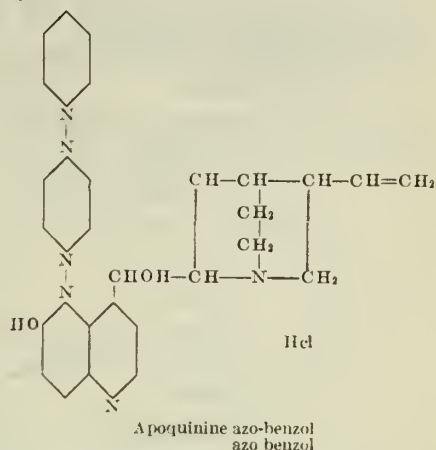
(4) In the similar way, if it is bound to hydrocupreine, crystals of deep red color are produced.

(5) If amino azo benzol disulphonic acid is diazotised and bound to hydro cupreine, red crystals are obtained.

Further, if amino azo benzol is diazotised and bound to chlor hydrocupreine, apoquinine chloride, hydrocupreine chloride and hydrocupreine iodide, a dye of deep red color of the property capable of dyeing fat is obtained. Moreover, by

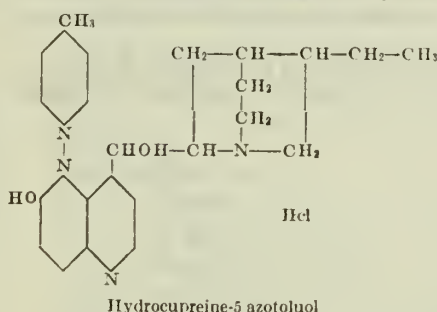
binding amino azo benzol to the before-mentioned cinchona alkaloid, azo compound is produced.

The formula of the typical reaction in this example is as follows:



Example III

If a compound obtained by substituting an



atomic group for amino benzol sulphonic acid and its sulphon amide and the hydrogen of its amide group or a compound obtained by substituting cyclic aromatic amine for amino group is diazotised and caused to act upon the before-mentioned cinchona alkaloid group, an anti-bacterial azo compound is obtained.

(1) If the above compounds are diazotised by 12 grams of sulphonic acid, 50 cubic centimeters of hydrochloric acid and 7 grams of sodium nitrite in the usual manner and bound to apoquinine, the red crystals of azo compound are produced.

(2) If 20 grams of para amino benzol sulphon amide is dissolved in 50 cubic centimeters of hydrochloric acid and 100 cubic centimeters of water and the solution is diazotised by 7 grams of sodium nitrite and then is caused to act upon 33 grams of hydro cupreine and 35 grams of caustic soda and bound to them, crystals of orange color of the melting point of 192° C. are obtained. Similarly, by binding para amino benzol sulphon amide to apoquinine, crystals of orange color of the melting point of 175° C. can be had.

(3) In the similar manner, if 23 grams of para amino benzol sulphon diethyl amide and dimethyl amide are diazotised and bound to apoquinine, crystals of orange color are obtained.

(4) By diazotising 35 grams of para amino benzol sulphon amide benzol sulphon amide in the usual manner and combining it with 30 grams of apoquinine, crystals of orange color of the melting point of 178° C. are got.

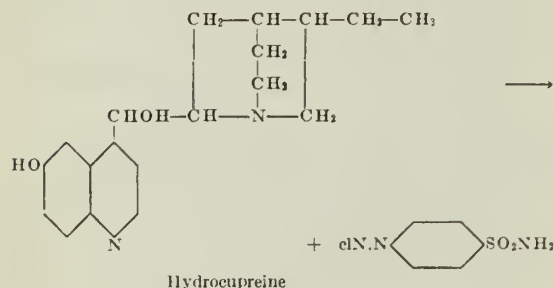
(5) Similarly, azo dye of orange color is obtained from hydrocupreine.

Further, if para amino benzol sulphon amide is diazotised by the usual process and bound to chlor hydro-cupreine, apoquinine chloride, hydrocu-

preine chloride and hydrocupreine iodide, the crystals of azo compound of orange color are obtained.

The product of this invention is not only anti-bacterial as already stated, but also is effective especially against streptococcus.

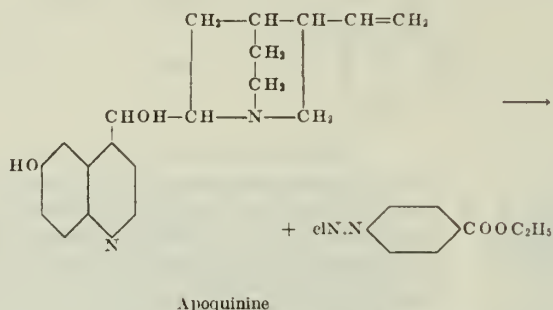
The following is the formula of the typical reaction in this example:



Example IV

If amino phenols are diazotised and made to act upon the before-mentioned cinchona alkaloid group, it is possible to obtain anti-bacterial azo compound.

(1) If 10 grams of para amino phenol, 30 cubic centimeters of hydrochloric acid and 100 cubic



centimeters of water are diazotised by 7 grams of sodium nitrite and are added and bound to 32 grams of hydro cupreine, 21 grams of caustic soda and 100 cubic centimeters of water, purple grey crystals of the melting point of 178° C. are obtained.

(2) Similarly, by binding 12 grams of 5-amino resorcline with hydrocupreine, purple grey crystals are obtained.

Example V

If aromatic carboxylic acid having amino group, its carboxylic acid amide and a compound with the hydrogen of its amide group substituted by an atomic group or a compound with the amino group substituted by cyclic amine are diazotised and caused to act upon the above-stated cinchona alkaloid group, anti-bacterial azo compound is produced.

(1) If 17 grams of para amino benzoic acid ethyl is diazotised by 7 grams of sodium nitrite and bound to 32 grams of apoquinine, crystals of dark brown color of the melting point of 210° C. are obtained.

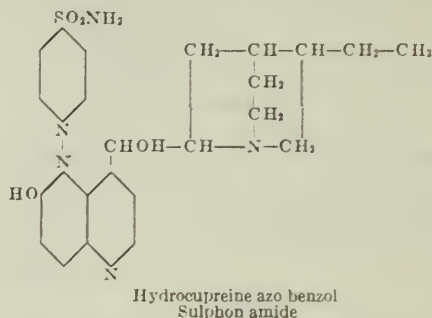
(2) In the similar manner, if 15 grams of para amino benzoic acid is bound to hydro cupreine, reddish brown crystals are obtained.

(3) By diazotising 15 grams of 5-amino salicylic acid and making it act upon apoquinine, crystals of dark pink color of the melting point of 188° C. are obtained.

(4) Similarly, if 17 grams of para amino cinamic acid is diazotised and bound to hydro cupreine, brown crystals are obtained.

(5) If 17 grams of para amino benzoic acid amide is diazotised and bound to apoquinine, crystals of reddish brown color are produced.

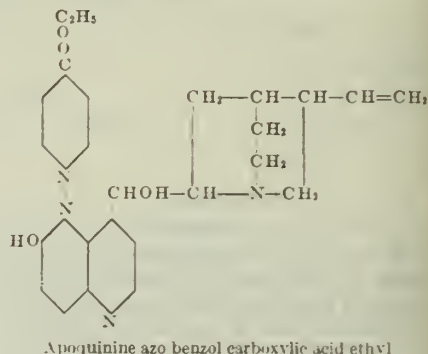
(6) If para amino benzoic acid diethyl amide is



diazotised and caused to act upon hydrocupreine, crystals of reddish brown color are obtained.

(7) If 17 grams of anthranilic acid is diazotised and bound to apoquinine, crystals of deep orange color of the melting point of 187° C. are obtained.

The following is the formula of the typical reaction in this example:



Example VI

If aromatic amines having a metal-containing atomic group as the group to be substituted are diazotised and bound to the before-mentioned cinchona alkaloid group, anti-bacterial azo compound is obtained.

The product of this invention has a special virtue for the diseases caused by spiro-worm.

(1) If 21 grams of para amino phenyl arsinic acid and 30 cubic centimeters of hydrochloric acid are diazotised by 7 grams of sodium nitrite and added and bound to a solution consisting of 32 grams of apoquinine and 21 grams of caustic soda, crystals of orange color of the melting point of 187° C. are produced.

(2) If para amino phenyl arsine is diazotised in the usual manner and bound to apoquinine, crystals of reddish orange brown color of the melting point of 225-230° C. are obtained.

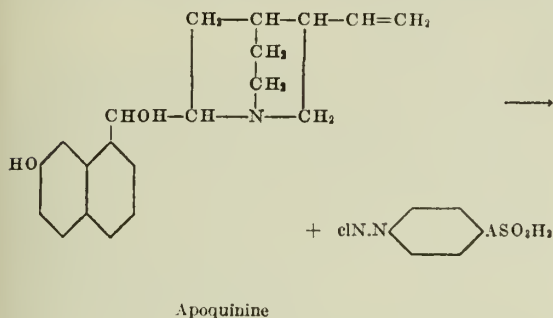
(3) By diazotising 3-amino-4-oxyphenyl 1-arsinic acid and binding it to hydro cupreine, crystals of reddish orange color of the melting point of 215° C. are obtained. In the similar way, if it is bound to apoquinine, crystals of the melting point of 174° C. are obtained.

(4) If 4-amino azo benzol 4-arsinic acid is diazotised in the usual manner and bound to apoquinine, crystals of orange color of the melting point of 165° C. are obtained.

Further, if 1 molecular weight of amino oxy-

phenyl arsen oxide, amino phenyl arsen oxide, amino thio-phenol, amino phenyl stibinic acid, amino oxyphenyl stibinic acid, amino oxyphenyl stibine oxide, amino phenyl arseno chlor-stibine, amino phenyl arseno chlor-bismuth and amino arsen phenyl stibinic acid are diazotised by the ordinary process and caused to act upon the before-mentioned cinchona alkaloids, for instance, hydrocupreine, anti-bacterial azo compound of orange color is obtained.

The formula of the typical reaction in this example is as follows:



Example VII

If cyclic amine belonging to amino diphenyls, amino naphthalenes, amino anthracenes, amino phenanthranes, amino pyridines, amino quinolines, amino pyrazolones, amino iso quinolines and amino acridines is diazotised and made to act upon the before-mentioned cinchona alkaloid and its derivative, antibacterial azo compound is obtained.

(1) If 20 grams of benzidine, 15 grams of sodium nitrite and 50 cubic centimeters of hydrochloric acid are diazotised in the usual manner and added to a solution consisting of 64 grams of apoquinine and 35 grams of caustic soda and combined with it, crystals of reddish purple color of the melting point of 185–190° C. are produced. In the similar way, from hydrocupreine is obtained crystals of dark reddish purple color of the melting point of above 200° C.

(2) 25 grams of ortho dianisidine, 15 grams of sodium nitrite and 50 cubic centimeters of hydrochloric acid are diazotised by the ordinary process and added to a solution consisting of 64 grams of apoquinine and 35 grams of caustic soda and combined with it, crystals of reddish purple color are obtained.

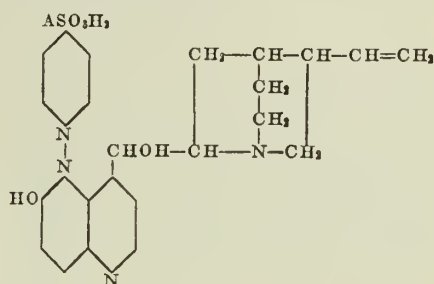
(3) If 20 grams of para amino diphenyl amine, 7 grams of sodium nitrite and 50 cubic centimeters of hydrochloric acid are diazotised in the usual manner and bound to apoquinine, crystals of darkish purple color of the melting point of 158° C. are obtained.

(4) If 15 grams of β -naphthyl amine, 7 grams of sodium nitrite and 50 cubic centimeters of hydrochloric acid are diazotised and added to a solution consisting of 32 grams of apoquinine and 35 grams of caustic soda and combined with it, crystals of light dark red color of the melting point of 128° C. are obtained.

(5) Similarly, from α -naphthyl amine is obtained crystals of dark red color of the melting point of 128° C.

(6) If 25 grams of 1-amino-2-naphthol-4-sulphonic acid is diazotised in the usual manner and made to act upon 32 grams of apoquinine, crystals of dark grey color of the melting point of 172° C. are produced.

(7) By diazotising 23 grams of naphthionic acid in the usual way and combining it with apoquinine, crystals of the melting point of above 200° C. are obtained.



Apoquinine azo phenyl arsenic acid

(8) If 20 grams of β -nitronaphthyl amine is diazotised in the usual manner and combined with 32 grams of apoquinine, crystals of light bluish green color of the melting point of 165° C. are obtained.

(9) By diazotising 23 grams of β -amino anthraquinone in the usual way and binding it with 32 grams of apoquinine, crystals of greyish orange color of the melting point of 161° C. are obtained.

(10) If 10 grams of α -amino pyridine is diazotised by the usual process and caused to act upon 32 grams of apoquinine, crystals of greyish red color of the melting point of 157° C. are obtained.

(11) If 18 grams of amino antipyrine is diazotised and made to act upon hydro cupreine, azo compound of dark grey color is produced.

(12) If 15 grams of amino quinoline and amino iso quinoline are diazotised in the usual way and caused to act upon 32 grams of hydro cupreine, brown crystals are obtained.

(13) If 27 grams of 3,6 diamino 10 methyl acridinium chloride, 50 cubic centimeters of hydrochloric acid and 7 grams of sodium nitrite are diazotised and made to act upon 32 grams of hydrocupreine, crystals of dark purple color of the melting point of above 200° C. are obtained.

(14) Similarly, from apoquinine are obtained crystals of the melting point of above 200° C.

(15) If 27 grams of 2. ethoxy 6.9 diamino acridine is diazotised in the usual way and made to act upon 32 grams of hydrocupreine, crystals of dark purple color of the melting point of above 200° C. are produced.

(16) In the similar way, from apoquinine are obtained crystals of the melting point of above 200° C.

TAKEO TAKAYANAGI.

ALIEN PROPERTY CUSTODIAN

COMPOUNDS HAVING VITAMIN B₆ ACTIVITY

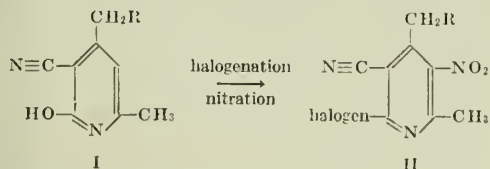
Otto Zima and Fritz Jung, Darmstadt, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed July 20, 1940

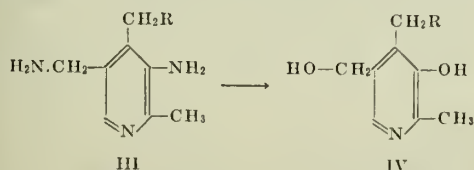
This invention relates to compounds having vitamin B₆ activity, intermediates used in their production, and to processes for such production.

Synthetic substances having the properties of vitamin B₆ in biological tests have not been heretofore known. Vitamin B₆ is obtained in small amounts from natural material by means of very troublesome procedures. It has not previously been obtained synthetically.

According to this invention, compounds with the activity of vitamin B₆ may be prepared from 2-methyl-3-nitro-5-cyano-6-halogen pyridines having in position 4 the group CH₂R, where R is hydrogen, hydroxyl or a group which may be converted into OH. These substances are easily prepared from acetyl acetone or its derivatives of the formula CH₃—CO—CH₂—CO—CH₂R₁, where R₁ is OH or a group which may be converted into OH, ammonia, and a suitable derivative of malonic acid or cyano acetic acid (such as malonic amide, permitting the subsequent conversion of the acid amide into the nitrile group; or cyanoacetic ester or its amide) which is adapted to permit formation of a pyridine nucleus. The stated reaction components may be allowed to react simultaneously, or the mono-imine may be first prepared from acetyl-acetone (or its derivatives) and ammonia, and then condensed with the malonic acid derivative. Compounds of formula I are thus obtained in good yields, which are converted into the desired starting material of formula II by nitration and halogenation.



The invention consists in reducing these compounds under such conditions that a substitution of the halogen by hydrogen and a reduction of the cyano- and nitro groups to aminomethyl and amino groups takes place, for which end catalytical reduction is particularly suited. Both amino groups of the compound III thus obtained may be substituted by hydroxyl groups, by the usual processes of diazotization and boiling.



The synthesis may be very easily and simply carried out as follows:

2,4-dimethyl-5-cyano-6-hydroxypyridine, eas-

ily obtainable from the imino compound of the acetyl acetone and cyano acetic ester, is nitrated, for example, with a mixture of concentrated sulfuric and nitric acid or with nitric acid and acetic anhydride. The nitrated compound is then chlorinated, for example, with thionyl chloride, phosgene, or POCl₃ and PCl₅, whereby 2,4-dimethyl-3-nitro-5-cyano-6-chloropyridine is obtained.

Surprisingly, this substance may be reduced catalytically in one operation to 2,4-dimethyl-3-amino-5-aminomethylpyridine. The catalytic reduction of a cyano group in the pyridine series has not been heretofore carried out, the reduction having been always carried out, in a troublesome way, by reducing chemicals, and with very poor results. Finally, both the aliphatic and the pyridine amino groups are transformed into hydroxyl groups in one operation by diazotization and boiling in an acid solution.

2,4-dimethyl-3-hydroxy-5-hydroxymethylpyridine thus obtained melts at 254° C. and, surprisingly, shows the biological activity of vitamin B₆.

We have also discovered that an alkoxyacetylacetone may be reacted with a cyanacetic acid ester to form 2-methyl-4-methoxymethyl-5-cyano-6-hydroxypyridine, and that upon nitration and chlorination of the latter compound, 2-methyl-3-nitro-4-alkoxymethyl-5-cyano-6-chloropyridine is obtained. The latter compound is hydrogenated to 2-methyl-3-amino-4-alkoxymethyl-5-aminomethylpyridine, which is diazotized to form 2-methyl-3-hydroxy-4-alkoxymethyl-5-hydroxymethylpyridine. The latter compound, upon treatment with hydrobromic acid, forms 2-methyl-3-hydroxy-4,5-di-(bromomethyl)-pyridine, which, upon hydrolysis, forms vitamin B₆.

The following examples illustrate methods of carrying out the present invention, but it is to be understood that these examples are given by way of illustration, and not of limitation.

Example I

2,4-dimethyl-5-cyano-6-hydroxypyridine is nitrated with concentrated sulfuric and nitric acid to the 2,4-dimethyl-3-nitro-5-cyano-6-hydroxypyridine. The 3-nitro derivative thus obtained is chlorinated with a mixture of POCl₃ and PCl₅. 2,4-dimethyl-3-nitro-5-cyano-6-chloropyridine, melting at 112° C., is obtained.

7.1 g. of 2,4-dimethyl-3-nitro-5-cyano-6-chloropyridine is dissolved in 200 cc. methanol and shaken with H₂ with the addition of 15.6 cc. 2NHCl in the presence of 5 g. of Pd-charcoal at room temperature. After 40 hours, 6 mol. of H₂ is absorbed, and the hydrogenation ceases. After filtering off the catalyst, the solvent is evaporated and the residue recrystallized from methanol and ether. The 2,4-dimethyl-3-amino-5-methyl-

aminopyridine crystallizes in the form of its dihydrochloride in white glistening platelets with a decomposition point of 310° C. Yield: 95% that of theory. The free base may be isolated by extraction of a concentrated alkaline solution of the dihydrochloride with chloroform, and melts at 132° C. after recrystallization from methanol and ether.

2.24 g. of 2,4-dimethyl-3-amino-5-methylaminopyridine dihydrochloride is dissolved in 10 cc. of water and treated with a solution of 1.5 g. sodium nitrite in 10 cc. water. 15 cc. of 1 N hydrochloric acid is added to this mixture while stirring. The reaction solution is kept for approximately 1 hour at 60° C. until no more nitrite can be determined with starch paper impregnated with potassium iodide. Then the solution is evaporated in vacuo and the well-dried residue is extracted several times with absolute alcohol. The residue remaining on the evaporation of the alcohol is recrystallized from methanol and ether, whereby 2,4-dimethyl-3-hydroxy-5-hydroxymethylpyridine in the form of the hydrochloride, melting at 254° C., is crystallized out.

In the vitamin B₆ test as a growth substance for lactic acid bacteria according to Möller [Zeitschrift für physiol. Chemie, 254, 285 (1938)] this substance shows indisputably positive activity from which the optimal concentration is placed around 17/cc.

Heretofore, no substance has shown activity in this test, other than the natural vitamin B₆.

Example II

2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine is prepared by condensation of methoxyacetylacetone with cyanoacetic acid ester in 25% ammonia at 60° C., 2-methyl-4-methoxymethyl-5-cyano-6-hydroxypyridine being obtained. This compound is first nitrated by means of 86% nitric acid in acetic anhydride at a temperature not higher than 60° C. to form 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-hydroxypyridine, and the latter compound is chlorinated with phosphorus pentachloride and phosphorus oxychloride by heating under reflux.

15 g. of 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine is shaken with hydrogen at room temperature in 600 cc. methanol with the addition of 31.5 cc. 2 N hydrochloric acid in the presence of 10 g. of 10% palladium charcoal. The absorption of 3 mol. of hydrogen proceeds rapidly with evolution of heat. In 15 hours the hydrogenation ceases after absorption of 6 moles of hydrogen. The catalyst is filtered off, the solvent is distilled off, and ether is added, whereupon 2-methyl-3-amino-4-methoxymethyl-5-amino-methylpyridine separates out in white needles. On recrystallization from methanol it melts at 236° C. The yield amounts to 90% of theory.

To a solution of 7.3 g. of 2-methyl-3-amino-4-methoxymethyl-5-methylaminopyridine-dihydrochloride in 50 cc. of water is added dropwise and while stirring a solution of 4.4 g. sodium nitrite in 50 cc. water and 29 cc. 2 N hydrochloric acid. The solution is kept at 60-70° for 30 minutes longer and finally is evaporated to dryness at 40° C. in vacuo. It is separated from the sodium chloride by extraction of the well-dried residues with absolute alcohol, and the solution obtained is evaporated in vacuo. The residue is recrystallized from absolute alcohol and acetone. Thus 2-methyl-3-hydroxy-4-methoxymethyl-5-hydroxymethylpyridine, as the monohydrochloride salt melting at 182° C., is obtained. Yield, 5 g.

The 4-methoxymethyl group of this compound may be easily converted by boiling with 66% hydrobromic acid. Since the hydrobromic acid attacks also the aliphatic hydroxyl group, 2-methyl-3-hydroxy-4,5-di-(bromomethyl)-pyridine is obtained, which may be converted into 2-methyl-3-hydroxy-4,5-di-(hydroxymethyl)-pyridine by treating it with boiling water, and then with silver chloride.

Other 4-alkoxymethylpyridines may be used in the process. For example, when employing ethoxyacetylacetone as a starting material, the corresponding 4-ethoxymethylpyridine will be obtained.

OTTO ZIMA.
FRITZ JUNG.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF DERIVATIVES OF PYRIDINE

Otto Zima and Fritz Jung, Darmstadt, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed July 20, 1940

This invention relates to a process for the manufacture of derivatives of pyridine.

The reduction of cyanopyridines to the corresponding aminomethylpyridines is a reaction on which much work has been done at various times, since considerable difficulties are encountered in that the usual reduction process for aliphatic or aromatic cyano groups is not effective with the cyano group attached to the pyridine nucleus. Thus, although aminomethyl compounds were early prepared by the reduction of aromatic or aliphatic cyano compounds, aminomethylpyridines were unknown until 1933. Camps [Arch. Pharm., 240, 370 (1902)] first tried to prepare these chemotherapeutically interesting substances by the reduction of cyanopyridine, using sodium amalgam as a reducing agent. However, instead of the hoped for compound, cleavage of hydrocyanic acid took place, together with saponification of the compound to the acid amide and then to the acid. With aluminum amalgam no better results were obtained.

Wibaut and Overhoff [Rec. trav. chim., 52, 55-6 (1933)] were the first to carry out the desired reaction although unintentionally. In attempting to convert the cyano group of 2,6-dichloro-4-cyanopyridine into the aldehyde group according to the method of Stephen, by treatment with stannous chloride and hydrochloric acid, and subsequent hydrolysis, they obtained surprisingly enough a straightforward reduction of the cyano group to the aminomethyl group. This process, however, can not be applied to other cyanopyridines. In an attempt to reduce 2-cyanopyridine according to this method, most of the starting material was recovered, and a small portion of it was hydrolyzed.

Graf [J. prakt. Chem. 140, 39 ff, (1934); 146 88 ff, (1936)] was the first to finally describe a process for the reduction of cyanopyridines, which has shown itself to be of general application up to the present time. In this process, chromium salts in an alkaline solution are used as reducing agents. This procedure is extremely troublesome and tedious, since it is dependent on the exact amount of the chromium salts used. With excess of salt, ammonia is split off, giving methylpyridines and, moreover, the yields are often less than 50%.

According to the present invention, the reduction of cyanopyridines to the corresponding aminomethyl compound occurs with 90% yields, and the elimination of the reducing agent and the working up of the mixture are quite simple. We have discovered that the reduction of a cyano-

pyridine with hydrogen in the presence of hydrogen carrying catalysts, particularly noble metal catalysts, proceeds surprisingly smoothly. although undesired results, such as the formation of secondary amines, nitrogen free substances or heterocyclic substances, have been observed with this reaction in other cyano compounds.

This new reduction process gives excellent results even with cyanopyridines having relatively complicated substituents. The reduction of the cyano group is not hindered, even though the compound to be reduced contains other groups such as halogen or nitro, which are also liable to catalytical reduction.

The catalytical hydrogenation of the cyano group can be carried out in solution with or without the addition of acid. The lower aliphatic alcohols, glacial acetic acid, diluted acids, etc., are suitable solvents. When the reduction is carried out at atmospheric pressure at room temperature, it ceases on the absorption of the theoretical amount of hydrogen (4 atoms hydrogen for each cyano group).

The compounds obtained according to the invention are used as medicinals or as intermediate products for the manufacture of medicinals.

The following examples illustrate methods of carrying out the present invention, but it is to be understood that these examples are given by way of illustration and not of limitation.

Example I

7.1 g. 2,4-dimethyl-3-nitro-5-cyano-6-chloropyridine (m. p. 112° C.) is dissolved in 200 cc. methanol with the addition of 15.7 cc. 2 N hydrochloric acid in the presence of 10 g. of 10% Pd-charcoal, and shaken with hydrogen at room temperature. On the absorption of 6 mol. of hydrogen, the hydrogenation ceases. The solution, filtered off from the catalyst, is evaporated almost completely and treated then with ether, 2,4-dimethyl-3-amino-5-aminomethylpyridine crystallizes out as the dihydrochloride in white shiny platelets, melting at 310° C. Yield, 95% of theory.

Crystalline 2,4-dimethyl-3-amino-5-aminomethylpyridine is isolated by extraction of a concentrated alkaline solution of the dihydrochloride with chloroform. On recrystallization from methanol and ether it melts at 132° C.

Example II

7.4 g. of 2,4-dimethyl-5-cyano-6-hydroxypyridine, (m. p. 291° C.) in 400 cc. of methanol and 5 cc. of concentrated hydrochloric acid ($d=1.19$)

is hydrogenated in the presence of 10 g. Pd-charcoal at 60° C. After 10 hours, 2 mol. of H are absorbed, and the hydrogenation ceases. After filtration of the catalyst, the solvent is evaporated almost completely, and the 2,4-dimethyl-5-aminomethyl-6-hydroxypyridine crystallizes out on the addition of ether as the hydrochloride in shiny platelets. On recrystallization from methanol and ether it melts at 320° C. Yield, 92% of theory.

Example III

1.7 g. of 2,4-dimethyl-3-amino-5-cyano-6-chloropyridine, m. p. 140° C. (obtained by the discontinuation of the hydrogenation described in Example I after the absorption of 3 mol. H) is shaken with hydrogen in methanol with the addition of 1 cc. of concentrated hydrochloric acid ($d=1.19$) at 60° C. in the presence of 0.5 g. of Pd-charcoal. Upon the absorption of 3 mol. of H, the hydrogenation ceases. The catalyst is filtered off with suction, the solvent is evaporated, and the residue is treated with ether. 2,4-di-

methyl-3-amino-5-aminoethylpyridine separates out as the dihydrochloride. On recrystallization from methanol and ether it melts at 310° C. Yield, 1.5 g.

Example IV

15 g. of 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine is shaken with hydrogen at room temperature in 600 cc. methanol with the addition of 31.5 cc. 2 N hydrochloric acid in the presence of 10 g. of 10% palladium charcoal. The absorption of 3 mol. of hydrogen proceeds rapidly with evolution of heat. In 15 hours the hydrogenation ceases after absorption of 6 moles of hydrogen. The catalyst is filtered off, the solvent is distilled off, and ether is added, whereupon 2-methyl-3-amino-4-methoxymethyl-5-aminomethylpyridine separates out in white needles. On recrystallization from methanol it melts at 236° C. The yield amounts to 90% of theory.

OTTO ZIMA.
FRITZ JUNG.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE EXTRACTION OF RESIN FROM TOMATO SKINS

Giovanni Mauri, Parma, Italy; vested in the
Alien Property Custodian

No Drawing. Application filed July 30, 1940

The present invention refers to a process for the extraction from tomato skins of resin which is particularly suitable for industrial application as in the manufacture of materials for flooring and lining e. g. wall covering.

The product obtained according to the process object of the present invention is particularly suitable for substituting linseed oil derivatives in the manufacture of fibrous elastic layers known under the trade-name "linoleum".

Tomato skins are thoroughly washed with water until all seeds and other foreign matters are removed therefrom, in order that there may

remain only the epithelial portion of the fruit which is then treated with hot or cold solution of caustic alkalies in water or in organic solvents.

5 The resin is thus transformed into a solution and the liquid portion is separated from the skins by filtration or decantation: the alkaline liquid obtained is neutralized or is acidified with mineral or organic acids. In such a way the resin is liberated and floats on the surface; then the same
10 is collected and washed with water until the reactive substances are completely removed and finally is dried.

GIOVANNI MAURI.

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Climate	3110
Weather	3115
Seismology	3120
Volcanology	3125

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF SYNTHETIC LINEAR CONDENSATION POLYAMIDES

Paul Schlack, Berlin-Treptow, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed July 31, 1940

This invention relates to new compositions of matter and more particularly to synthetic linear condensation polyamides and to filaments, fibers, yarns, fabrics and the like prepared therefrom.

By heat-condensation of bifunctional polyamide-forming components like amino carboxylic acids and their derivatives, for instance esters, amides, lactams, formyl compounds, urethanes or mixtures or salts of equivalent portions of one or several diamines and one or several dicarboxylic acids or mixtures of functional derivatives of the acids, for instance esters, amides and dicarboxylic acids or derivatives of the amines, for instance formyl compounds, N'-carboxyl-alkyl-substituted primary amino compounds and dicarboxylic acids, synthetic resins or artificial materials of very high molecular weight are obtained, when the components are so chosen, that tendency for the formation of hetero rings, especially with 5 and 6 ring members, does not exist or to a very small extent only.

Also mixtures of various amide-forming bifunctional compounds, for instance of amino acids or of a pair of substances, especially diamines and dicarboxylic acids, were condensed together, for instance two or several various amino acids for themselves or amino acids or derivatives of such acids, for instance lactams with one or several salts obtained from diamines and dicarboxylic acids. There were obtained mixed condensates with properties diverging in many cases from those of uniform compounds.

In these cases the condensation reaction cannot be entirely foreseen, because it depends on the reaction velocity of the single components or the reactants at the respective temperature, which of the components react preferably and which of them come into reaction later and slower. In the extreme it may happen that an amid-forming component reacts first entirely nearly by itself. As a rule the irregular mixed condensates show increased transparency and solubility compared with the uniform products, whereby the melting point simultaneously decreases. On the other hand formed structures prepared therefrom show usually after the cold-drawing or -rolling a somewhat lower degree of orientation than the uniform polyamides.

This invention has as an object the preparation of new and valuable compositions of matter, particularly synthetic fiber-forming materials.

A further object is the preparation of filaments, fibers, ribbons and foils from these materials.

A further object is to form these materials by

casting, dye-casting, injection moulding or rolling into useful matters.

A further object is the manufacture of yarns, fibers and the like from said filaments.

Further objects will become apparent from the detailed specification following hereinafter.

It has been found that very valuable condensation- and mixed condensation products, which differ in their properties from those obtained by direct condensation of the same fundamental components, are obtained, when the condensation wholly or in part is carried out with bifunctional components adapted for amid formation, the chain of which contains already CO—NR—groups (R=H or a monovalent organic radical) stable at reaction temperature and which are, if necessary, interrupted by other hetero atoms or atom groups like O, S, N, SO, SO₂. By CO—NR—groups, practically stable at reaction temperature, such amino groups are to be understood, which do not react in the condensation mixture under separation of a carbonyl group. Urethane compounds derived from primary amino groups, which consequently react in the presence of carboxyl compounds by splitting off alcohol and carbon dioxide, are intentionally excepted here as components according to the present invention, provided they do not contain the stable—CO—NR—group in the chain.

By fundamental components there are meant the simple building stones in which the polyamides are split up by acid hydrolysis.

Preferably the components according to the present invention are used as much as possible in a uniform state. In order to obtain special effects, for instance with regard to solubility, any mixture may be used for condensation, provided that the functional groups are present in the equivalent proportion necessary for polyamid formation. As the substances containing already amid groups in most cases are very little or not at all volatile, advantages result during the practice of the condensation; quite often it is unnecessary to use pressure vessels. Besides the components containing amid groups in the chain also numerous other substances or pair of substances suitable for polyamid formation in the heat may be present in the mixture, for instance amino carboxylic acids and functional derivatives of such acids like ester, amides, lactams, formyl compounds, N-carboxyl alkyl compounds or salts from diamines and dicarboxylic acids or mixtures from derivatives of diamines and dicarboxylic acids or from derivatives of dicarboxylic

acids with diamines suitable for polyamide formation between each other.

Also finished polyamides which may be transformed into higher molecular products by after-condensation may be added to the reaction mixture.

The components according to this invention may be bifunctional containing two identical radicals, for instance two COOH-groups, i. e. for instance they may be substituted twice by an amino group or by a carboxyl group. As will be shown later on such compounds are synthetically obtainable in many ways, especially symmetrically built compounds which are generally to be preferred. But also bifunctional compounds with two different radicals, for instance amino carboxylic acids, are within the scope of the present invention, though bifunctional compounds of the same character are easier obtainable as a rule. Instead of compounds with amino groups and carboxyl groups besides amide groups, also functional derivatives of them may be used, for instance esters with low alcohols or phenols, formyl amino compounds and urethanes derived from primary amino compounds.

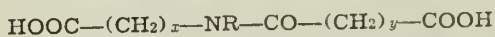
Typical reactions used for the synthesis of components according to this invention are contained in the examples and arranged in the following table.

TABLE

Uniform bifunctional components containing amide groups in the chain.

(I.) COMPOUNDS WITH ONE AMIDE GROUP

(a.) Dicarboxylic acids.

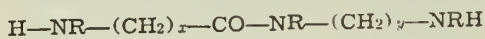


x at least=5, y at least=3, better 4 or more,
R=monovalent organic radical, especially alkyl.

Example

Reaction product from methylester adipic acid chloride with ϵ -amino caproic acid, if desired alkaline saponification into the dicarboxylic acid.

(b.) Diamine.

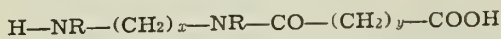


x =at least 5, y =at least 4.

Example

Reaction product of the carboxyethyl- ϵ -amino caproic acid chloride (from the acid with thionyl-chloride) with mono-carboxyethyl-hexamethylene diamine (the latter being obtained by action of chloroformic acid ethylester on excess hexamethylene-diamine). The diurethane is directly condensable with dicarboxylic acids.

(c.) Amino carboxylic acid.



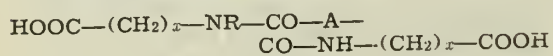
x at least=4, y at least=3, better 4 or more.

Example

Reaction product of one mol glutaric acid with one mol hexamethylene diamine in benzene.

(II.) COMPONENTS WITH TWO AMIDE GROUPS

(a.) Dicarboxylic acids.

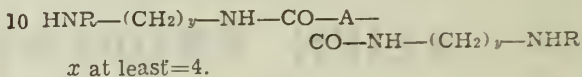


x =at least 5, A=bivalent organic radical, which in the simplest case may be=0.

Example

Oxalyl-bis-amino caproic acid. Instead of the oxalic acid also its homologs or analogs may be used, for instance malonic acid, glutaric acid, adipic acid, sebacic acid, γ -thio-dibutyric acid, γ -oxydibutyric acid, aromatic dicarboxylic acids like terephthalic acid, isophthalic acid.

(b₁.) Diamino compounds.

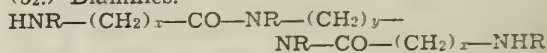


x at least=4.

Example

Reaction product from oxalic acid diethylester and N-monomethyl-hexamethylene diamine. Preferably such components are suitable for the condensation, which are onesided monosubstituted for instance by an alkyl radical, an acyl radical, for instance formyl- or carboxyl radical, which latter do not disturb the reaction. Instead of the oxalic acid also other dicarboxylic acids may be used as described under a. In the same manner the diamine may be replaced by diamino compounds with hetero atoms interrupting the chain, for instance by $\beta\beta$ -diamino diethylether or $\beta\beta$ -diamino diethylsulfide.

(b₂.) Diamines.

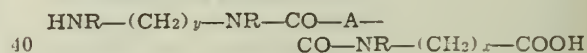


x =at least 5, y =at least 4.

Example

Reaction product from two mols N-monomethyl- ϵ -amino-caproic acid methylester with one mol hexamethylene diamine (in the presence of a small amount of sodium ethylate).

(c.) Amino carboxylic acids.



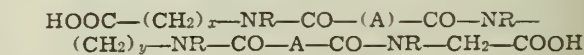
x =at least 5, y =at least 4.

Example

ϵ -amino caproic acid is caused to react with excess oxalic acid di-ethylester and the obtained N-methylester oxalyl caproic acid is caused to react with N-monomethyl pentamethylene diamine.

(III.) COMPONENTS WITH MORE THAN TWO AMIDE GROUPS

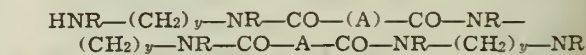
(a.) Dicarboxylic acids.



Example

Hexamethylene diamine is caused to react with excess oxalic ester into the bis-oxamide acid ester. The latter is condensed with ϵ -amino caproic acid ester in alcohol solution and then saponified in alkaline solution.

(b.) Diamines.

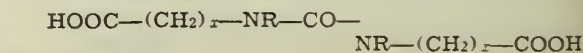


Example

Hexamethylene-bis-oxamide acid ester is condensed with two mols monomethyl hexamethylene diamine.

(IV.) COMPOUNDS WITH ONE UREA RADICAL

(a.) Dicarboxylic acids.



x =at least 5.

Examples

Carbonyl-bis- ϵ -amino caproic acid.

Carbonyl-bis-NN'-dimethyl-amino caproic acid. (Obtainable from the amino acid esters with phosgene or diphenyl carbonate and following saponification.)

(b.) Diamines.

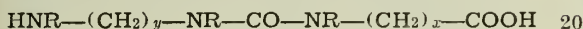


$y=4$ or more.

Example

Reaction of N-carboxyethyl-N'-monomethyl hexamethylene diamine with phosgene. The diurethane is directly condensable with dicarboxylic acids. The thermal resistance is increased by methylation of the urea-nitrogen-atoms.

(c.) Amino carboxylic acids.

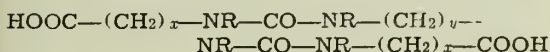


Example

Condensation of carbamic acid phenylester- ϵ -amino caproic acid methylester with NN'-dimethyl hexamethylene diamine.

(V.) UREA DERIVATIVES CONTAINING MORE THAN ONE UREA-GROUP IN THE MOLECULE

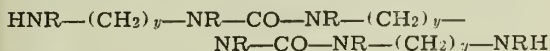
(a.) Dicarboxylic acids.



Example

NN'-dimethyl hexamethylene diamine is transformed with phosgene into the hexamethylene diamine-bis-carbamic acid chloride. The latter is coupled with ϵ -amino caproic acid or 9-amino nonanoic acid.

(b.) Diamines.



Example

Hexamethylene-bis-carbamic acid chloride is condensed with N-carboxyethyl-hexamethylene-diamine.

The above table which is in no way considered to be complete, shows, how extensively the components according to this invention may be transformed. The invention, however, is not limited to the types mentioned there and to the components described in the examples. Within the scope of this invention lies also, generally speaking, the use of bifunctional components adapted for polyamide-formation, the chains of which are interrupted by amide groups (urea groups) once or several times, for the manufacture of high molecular polyamides with preferably linear structure. Excepted are here only simple urethane compounds derived from primary amines, whereas urethanes from secondary amino compounds, for instance diurethanes from NN'-dimethyl-hexamethylene diamine or urethanes from secondary amino carboxylic acids, for instance from N-methyl- ϵ -amino caproic acid are within the scope of this invention. Of the secondary urethane compounds are those especially reactive in which the carboxyl is esterified with an aromatic or enolic hydroxyl compound, for instance with phenol, phenol homologs or halogenated phenols like p-chloro-phenol or p-chloro-m-cresol.

In the cases mentioned in the table bifunctional compounds were built up with amide

groups from bifunctional starting materials. However, it is also possible to introduce the final end-groups by other groups being not reactive in the sense of the final product, for instance by exchange of reactive halogen against amino or nitrile groups, by reduction of nitrile groups or nitro groups or by oxidation of for instance hydroxyl groups.

Especially valuable are starting materials which contain already prepared two or more amide groups, for instance the dicarboxylic acids easily obtainable which consist of a central dicarboxylic acid radical and two amino acids on each side. As central dicarboxylic acid the inexpensive oxalic acid is besides others especially useful. With the aid of this component it is also possible to increase sometimes considerably the melting point. Especially such diurea compounds are easily accessible besides the simple urea dicarboxylic acids, which show as central member the radical of a diamine. Thermally especially resistant are ureas containing alkyl groups, especially methyl groups on the nitrogen atom.

Only two components are preferably used for the condensation, if it is intended to prepare uniformly built polyamides. By condensing another component into the polyamide, the radical of which is not yet contained in the bifunctional compound with amide groups, very valuable, uniform mixed-polymerisates are obtained. The uniform mixed-condensates consisting of more than two functional components are more valuable for many purposes, for instance for the manufacture of artificial filaments, than those being irregularly built, which, however, in another respect possess advantages. By mixing the polyamides in various proportions, the properties may be extensively varied.

The condensation of the bifunctional compounds according to the present invention with themselves or with other components containing opposite or supplementary functional groups is accomplished in the usual manner, i. e. by heating to reaction temperature in the presence or absence of solvents or diluents, for instance phenols, glycols, low alcohols and water. One may work partly at atmospheric pressure and, if necessary, partly at increased or reduced pressure. The temperature suitable for the reaction is easily found in every case by pre-tests. It lies as a rule between 150 and 280° C. When using very reactive reactants, for instance carboxylic acid arylesters, carbamic acid arylesters or isocyanates, already at temperatures below 150° C. very valuable condensation products are obtained. This is important, if components liable to decompose or to give side-reactions are present, for instance sulfo compounds like $\beta\beta'$ -diaminodithyl-sulfide or dicarboxylic acids tending to form cyclic monomers like glutaric acid.

In order to protect delicate components, the condensation may also be carried out according to U. S. Patent application Ser. No. — (corresponding to the German Patent application I. 64 092 IVd/12 o) exclusively or during the greater part of the reaction time in absence of solvents below the melting point of the reaction product.

Within the scope of this invention there lie also the condensations with bifunctional compounds which besides or instead of acyclic or exocyclic amide groups show hetero rings interrupting the chain with cyclic-bound amide groups, according to German Patent Application I. 64 527 IVc/12p, filed May 6, 1939. Other com-

ponents reacting by themselves in the heat under amide-formation may be present besides the components containing amide groups or their combinations with bifunctional compounds (reactive with identical or different radicals), for instance ω -amino carboxylic acids and functional derivatives of such like esters, amides, formyl compounds, N-carboxylic acid compounds derived from primary amino compounds, nitriles, lactams, salts of diamines and dicarboxylic acids, also equivalent portions of reactive derivatives from diamines and dicarboxylic acids or of reactive derivatives from dicarboxylic acids with diamines.

To increase the pressure or to accomplish hydrolytic, alcoholic or aminolytic processes, for instance in the presence of esters, nitriles or lactams, the addition of water, alcohols or also ammonia may be of advantage. One works then with more or less high pressure and finishes up finally the condensation under atmospheric pressure or reduced pressure, thereby eliminating the volatile ingredients of the reaction mixture.

To increase or regulate the reaction, especially to determine the final degree of polymerisation, there may be added in small quantities acid compounds or compounds splitting off acid or alkaline agents, for instance hydrochloric acid, phosphoric acid, naphthalene sulfo acid, salts of amines with strong acids, stannous chloride, magnesium alcoholates, alkali phenolates, especially such consisting of alkyl-substituted phenols. Furthermore there may be added compounds forming neutral or relatively feeble acids or alkaline end-groups to determine the degree of condensation, for instance mono- and dicarboxylic acids, mono- and polyamines, phenol esters of monocarboxylic acids, amides, glycols. The quantity of the amide forming admixtures has to be chosen in such a way, that the equivalent proportion is very little overstepped in one or the other direction.

The high molecular condensation products obtained according to the present invention may be used in various ways according to their properties. High polymeric polyamides may be worked up from the melt or from the solution, for instance in phenol, formic acid, acetic acid, in some cases also alcohols, into filaments, ribbons or foils and the like. They may be also formed by dye-casting, spraying or pressing in every way. Lower polymeric compounds for instance are suited for the manufacture of coatings and impregnations.

Example I

Two mols ϵ -amino caproic acid ethyl ester are caused to react in three parts absolute alcohol with 1 mol oxalic acid diethyl ester at 30° C. A great deal of the reaction products—oxalyl-bis- ϵ -amino caproic acid diethyl ester—is separated in flat long needles (f. p. 111° C.). The rest is distilled off and the residue taken up with water for purification. The substance may be recrystallized from alcohol.

This ester is saponified in boiling alcohol by gradually discharging the calculated amount of aqueous alkaline liquor into it. The alcohol is distilled off, the reaction product dissolved in water and the oxalyl-bis-amino caproic acid (f. p. 178° C.) is precipitated with hydrochloric acid.

Oxalyl-bis- ϵ -amino caproic acid (f. p. 178° C.) is transformed with the roughly calculated amount of hexamethylene diamine in 60 per cent alcohol into the difficultly soluble salt (f. p. 240°).

This salt is melted in a nitrogen atmosphere at 240° C. The temperature is then raised after one hour to 250° C. and kept there four more hours. A nearly bubble-free clear viscous melt is obtained after that time which, when cooled down, solidifies into a transparent, feebly colored resin. The polyamide melts at 185° C. and may be drawn from the melt into fine fibers or bristles which can be oriented by cold drawing. The condensation product is much harder than the polyamide from amino caproic acid or ϵ -capro lactam (f. p. 211–213° C.).

Example II

ϵ -amino caproic acid ethyl ester is caused to react, while cooling, with phosgene in toluene. There is obtained in good output the carbonyl-bis-amino caproic acid diethyl ester (f. p. 118° C.). By saponification with aqueous alcoholic alkaline liquor in a little more than the calculated amount at 40° C. the dicarboxylic acid is obtained (needles from alcohol, f. p. 162–164°).

The acid in aqueous alcohol is united with the calculated amount of hexamethylene diamine and the salt thus formed is isolated.

A part of the salt is heated in a nitrogen atmosphere at 180° C. for three hours. The temperature is then raised to 200° C. and kept another five hours at that temperature. After that relatively short time of heating, at moderate temperature, the substance could be drawn into filaments easily to be oriented.

The same polyamide is obtained when the ester is condensed with the diamine. In this case it is useful to heat first for two hours in a sealed vessel, then the reaction product is further heated after evaporation of the alcohol at atmospheric pressure in a nitrogen atmosphere at 220° C. for still nine more hours.

Example III

One mol hexamethylene diamine is heated up in one part alcohol (by weight) with two mols cyanoacetic acid methyl ester for one hour on the water bath. When cooled down, the mass solidifies to a crystalline product NN'-dicyanoacetyl hexamethylene diamine. This dinitrile may be easily hydrolyzed with alcohol and hydrochloric acid over the imino ether to hexamethylene-bis-malonic acid diethylester amide ($\text{H}_5\text{C}_2\text{OOCCH}_2\text{COHN}(\text{CH}_2)_6\text{NHOCCH}_2\text{COOC}_2\text{H}_5$). If this ester is heated in xylenol with the equivalent amount octamethylene diamine for 6–12 hours at 225° C., a polyamide is obtained which can be spun. The malonic ester amide is also obtained by a reaction of hexamethylene diamine with malonic ethylester acid chloride.

Example IV

Two mols sodium salt of the sebacic acid monomethyl ester and one mol hexamethylene diamine are heated at 100–130° C. with diethylene glycol until no methanol distills off. After removal of the glycol in vacuo the product is dissolved in water and the dicarboxylic acid precipitated with hydrochloric acid. If this is heated with the equimolecular amount octamethylene diamine for 8 hours at 210–230° C., a polyamide capable of being spun is obtained, if the product is worked up in the usual manner. The reaction product is not identical with the polyamide obtained when condensing together two mols sebacic acid, one mol hexamethylene diamine and one mol octamethylene diamine.

Example V

Two mols NN'-dimethyl hexamethylene diamine in benzene are condensed with one mol chloroformic acid-xylenylester (from technical xynol) and the hexamethylene-bis-methyl carbamic acid xylenylester is also condensed in the proportion one mol:one mol with octamethylenediamine at 210° C. (the amino hydrochloride formed as by-product is separated off) until the viscosity of the melt is not increased any more. After diluting with xynol the reaction product is precipitated with alcohol. The polyamide thus obtained is soluble in strong formic acid and may be cast into foils from this solution.

Example VI

One mol glutaric acid dichloride is boiled with two mols N-methyl aminocaproic acid ethylester hydrochloride, obtained by esterification of methyl aminocaproic acid with hydrochloric acid and alcohol, in benzene until the development of hydrogen chloride is finished. The solvent is distilled off and the residue saponified with alcoholic aqueous caustic soda solution. The dicarboxylic acid thus obtained is heated with one mol octamethylene-bis-carbamic acid diphenylester at 200° C., whereupon polyamide-formation quickly results by splitting off phenol and carbondioxide. The mixture is carefully heated until the viscosity does not increase any more, dissolved in phenol and precipitated with acetone. The product may be spun into filaments from the melt. Also the analogous product from amino caproic acid can be spun. The polyamide containing methyl-substituted amide groups is thermally more resistant.

Example VII

One mol sebacic acid methylester acid chloride (obtained from the ester acid with thionylchloride) is boiled with one mol hydrochloric ϵ -amino caproic acid methylester in benzene, until the development of hydrogen chloride is finished. The benzene is distilled off and to the residue there is added one mol hexamethylene diamine. The whole is then heated in a sealed vessel at 230° C. for 2½ hours. After removal of the excess pressure the temperature is raised at 250° C. and kept there for 7 hours. The polyamide thus obtained may be drawn into fine filaments directly from the melt. It is not identical with the product obtained, if one mol neutral salt of sebacic acid and hexamethylene diamine is condensed under similar conditions with one mol ϵ -caprolactam.

Example VIII

Two mols ϵ -amino caproic acid dimethylester and octamethylene diisocyanate are united in benzene and the dicarboxylic acid ester obtained under evolution of heat, the chain of which is interrupted by the radical of the octamethylene diurea, is condensed after adding xynol with a further mol octamethylene diamine at 230° C. The reaction product is first heated on hour in a sealed vessel, then 7 hours under atmospheric pressure in a nitrogen atmosphere. The reaction product is isolated by precipitating with alcohol. By pressing hard structures are obtained.

Example IX

One mol bis- ϵ -amino caproyl hexamethylene diamine is heated with one mol ethylene carbamide-NN'- γ -dibutyric acid (according to German Patent Application I. 64 527 IVc/12p, filed May 6, 1939) in two parts xynol at 220° C. After 7

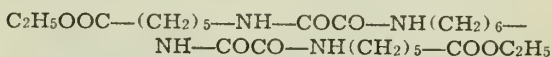
hours the polyamide thus formed is precipitated after diluting with a further amount of xynol by discharging it in acetone. The product is remelted under exclusion of atmospheric oxygen and may be drawn into filaments directly from the melt.

Example X

ϵ -amino caproic acid methyl ester in methylene chloride is transformed with the aid of chloroformic acid xylenyl ester into methyl carbamic acid xylenyl ester-N- ϵ -caproic acid methyl ester. This is heated with 1 mol hexamethylenediamine at 100° C. first for one hour, the temperature is then raised after sealing the reaction vessel at 200° C., then heated for 2 hours under pressure, the pressure reduced and condensed further 4 hours at 220° C. The reaction mass is worked up with acetone. Instead of hexamethylenediamine also piperazine may be employed for condensation.

Example XI

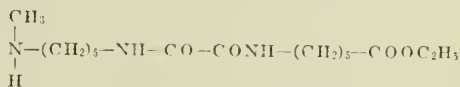
Hexamethylene diamine is discharged into a 30% alcoholic solution in excess of oxalic acid diethyl ester. After leaving at room-temperature hexamethylene-bis-oxamic acid diethyl ester (f. p. 89°) is formed in good output. This ester reacts at 30–40° C. very easily in alcoholic solution with 2 mols ϵ -amino caproic acid ethyl ester under formation of the dicarboxylic acid ester of the formula



This ester may be condensed by itself or after saponification with alcoholic aqueous alkaline liquor in the presence of xynol with the equivalent amount octamethylenediamine. In the first case the mixture of the components is first heated for one to two hours in a sealed vessel at 200–210° C. and then after releasing the pressure in a nitrogen atmosphere still further 9 hours at 230° C. In the second case it is condensed for 8 hours at 225–230° C. in a nitrogen atmosphere.

Example XII

ϵ -amino caproic acid ethyl ester is discharged into excess oxalic acid diethyl ester in alcohol and the solution is heated at 60° C., until the alkaline reaction disappears. Thereby is formed, nearly exclusively, the oxamide acid ethyl ester-N- ϵ -caproic acid ethyl ester which may be easily separated from a small quantity of in alcohol difficultly soluble oxal-bis-amino caproic acid ester formed as by-product in small quantity. If the oxamide acid ester is caused to react with the equivalent amount N-monomethyl pentamethylenediamine (from ϵ -chloro amyl benzamide and methylamine with following hydrolysis), the amino acid ester of the following formula is obtained in good output

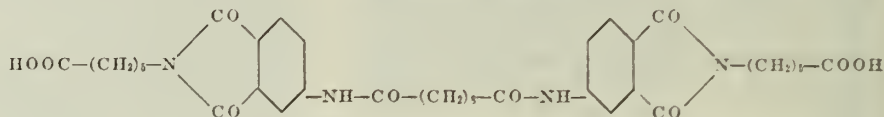


After saponification with aqueous alcoholic alkaline liquor the amino acid yields after heating in xynol at 225° C. for 12 hours a polyamide which can be spun.

Example XIII

One mol NN'-bis- ϵ -amino caproyl hexamethylenediamine is heated with one mol m-benzene disulfo-bis- ϵ -amino caproic acid (crystallizing with water in laminae, f. p. 173–174°) in xynol for 7 hours at 220° C. The reaction product purified

from xyleneol by reprecipitating is soluble in diluted caustic soda solution and is precipitated by acetic acid. The raw product may be dissolved also directly in the alkaline liquor, acidified with acetic acid and liberated from xyleneol by steam distillation. The product may be added to alkaline cellulose solutions, for instance solutions of alkali-soluble cellulose ethers, and may be coagulated together with them.



Example XIV

A warm solution of excess hexamethylene-bis-carbamic acid diphenyl ester (f. p. 138°) in benzene is discharged, while stirring into N-methyl-amino caproic acid methylester, also dissolved in benzene. The ester thus formed of the formula



is transformed by saponification with aqueous baryta solution and by following removal of the barium with the aid of sulfuric acid into ω-amino hexyl carbaminy-N-methylamino caproic acid. The acid may be easily condensed in xyleneol into a polyamide which may be spun into filaments directly from the melt.

The dicarboxylic acid ester may be condensed also with bivalent amines, for instance NN'-dimethylhexamethylenediamine. The use of secondary bases is of advantage in this case, as the urethanes or isocyanates derived from primary amino compounds yield urea compounds which may be retransformed in the heat. Besides that, the danger of net-formation is avoided by using secondary amino groups.

Example XV

2 mols 5-aminophthalic acid are coupled in

alkaline solution with 1 mol sebacic acid chloride. The tetracarboxylic acid separated with the aid of acids is transformed into the anhydride by heating in vacuo. The calculated amount (2 mols) 2-amino caproic acid is added to the molten anhydride (1 mol) and the mixture carefully heated, until the separation of water is finished. The dicarboxylic acid thus obtained of the following formula

15 is condensed in xyleneol with octamethylene diisocyanate in the proportion 1mol:1mol. By splitting off carbondioxide a high molecular polyamide precipitable with acetone is obtained. The polyamide becomes water soluble by heating with diluted caustic soda solution under cleavage of the imide groups.

By using diisocyanates as coupling components the danger of splitting up the imide rings during the condensation is avoided.

Example XVI

In a sealed vessel, in which the air is replaced by carbondioxide, exactly equivalent proportions of hexamethylene-diisocyanate and oxalyl-bis-ε-amino caproic acid are heated in the beginning at 200° C, until no further rise of pressure occurs. The formed carbondioxide is then carefully removed and the mixture is heated at 230° C. for two more hours without pressure. The mixed polymerisate thus obtained may be formed directly from the melt into filaments which can be drawn in the cold.

As there is no humidity present in the reaction mixture hydrolytic by-products are not formed. A product is therefore obtained, in which a very regular structure formation must be assumed.

PAUL SCHLACK.

ALIEN PROPERTY CUSTODIAN

PROCESSES FOR THE MANUFACTURE OF
ARTIFICIAL TEXTILE FIBRES

Antonio Ferretti, Milan, Italy; vested in the
Alien Property Custodian

No Drawing. Application filed July 31, 1940

This invention concerns improvements in or relating to processes for the manufacture of artificial textile fibres.

Casein which has been produced by known methods is unsuitable for the subsequent treatment required during the manufacture of artificial textile fibres. In order to obtain a suitable form of casein it has been found necessary to coagulate the milk with a quantity of acid in excess of that normally employed.

According to the present invention there is provided in a process for the manufacture of artificial textile fibres, the step of preparing casein by the acid treatment of milk at a pH value less than 4.5.

The casein thus obtained is suitable for use in the manufacture either of textile fibres which are equivalent to natural wool, or when mixed with viscose, of mixed fibres having characteristics ranging between those of natural wool and of cotton. It is possible to add mineral substances such as colloidal metal solutions or finely divided metal oxides or dioxides to the casein in order to impart particular qualities to the resultant fibres.

The following example indicates typical quantities of milk and acid which may be employed in order to obtain coagulation at the required pH value:

100 litres of skimmed milk at a temperature of 20° C. are treated with 250 cubic centimetres of 66° Bè. sulphuric acid. The acidity of the serum

at the moment of coagulation is equal to 2.9-3 pH. A casein is obtained which can readily be converted into artificial textile fibres.

The acid employed is given by way of example only and any mineral or organic acid or combination thereof may be employed, the quantity thereof being varied according to the degree of concentration and to the greater or smaller neutralising power of the acid or acids, it being understood that it is necessary to effect coagulation with an excess of acid as indicated above in connection with sulphuric acid, that is at a pH value within the specified limit.

Casein of the desired quality can also be produced from casein obtained by known processes by acid treatment of milk at a pH value in excess of 4.5 by subjecting it to a further acid treatment at a pH value below 4.5 in order to compensate for the insufficient quantity of acid employed at the moment of coagulation.

The specification of my co-pending U. S. Patent application Serial N. 96,470 claims a process for the manufacture of artificial textile fibres consisting essentially of casein one of the steps of which is claimed generally in the present specification. The following claims are to be read as excluding the use of this step in the complete process which is the subject of co-pending application Serial N. 96,470.

ANTONIO FERRETTI.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF HARDENABLE ORTHO-CRESOL ALDEHYDE CONDENSATES

Bernhard Habraschka, Hamburg, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed August 1, 1940

This invention relates to a process of producing a hardenable light-colored orthocresol aldehyde condensate.

Orthocresol aldehyde condensates are used only to a limited extent as mixed products with phenol aldehyde resins or urea resins in the manufacture of plastics, chiefly because their labile structure renders them inferior. They begin to set only under difficulties, or not at all, and it is equally difficult to bring about the completion of the setting process owing to the decomposition of the resin molecules. Furthermore, as the solubility of these products is much restricted, it will be understood that the use of orthocresol aldehyde condensates is at present practically nil.

The invention proposes to provide a process for the preparation of an orthocresol condensate which is free from the troubles mentioned and in its applicability is equal to high-grade phenol aldehyde condensates.

The process according to the invention is carried out by condensing o-cresol with an aldehyde in the presence of an ester of phosphoric acid and of a paraffin derivative of the C_9 — C_{18} group, e. g. their respective fatty acids or the esters thereof. Excellent results were obtained with a mixture of fatty acids as yielded during paraffin oxidation. By repeated fractionating, this mixture may be divided into three portions, each substantially comprising a mixture of fatty acids of the C_9 — C_{12} series, or if the C_{12} — C_{15} series, or of the C_{16} — C_{18} series.

The resulting products can serve already as plastic mass for pressing or as raw material for varnishes. Externally, they resemble so-called hard resin and are thermosetting.

It has further been found that these products can be materially improved by condensing and esterifying them with glycerides of oleic acid, preferably of myristic and eleo-margaric acids, and an agent combining with the free organic acids, as polyglycols, until the condensate becomes clear. The final product may be used in the form of a solid resin for the manufacture of plastics, etc. or serve in solution for making varnishes.

In its improved form the product can be hardened at lower and higher temperatures.

It was finally found that the product prepared in the manner indicated can be rendered polymerizable by dissolving it in a mixture of aliphatic and aromatic solvents and esters and mixing it with metal soaps, as metallic compounds combined with naphthenic, oleic or resin acids. These metal soaps may be added also after com-

pletion of condensation and the products worked in solid form.

According to the invention, high-grade products can be obtained whose properties are equal to those of pure phenol aldehyde condensates. It is possible for instance to prepare products which can be hardened at different temperatures within a range from 100–220° C., depending on use. The final product is soluble in the usual organic solvents and can therefore serve also for making high-grade varnishes, its stability being such that hardening is possible even at particularly high temperatures without decomposition of the resinoid molecule.

The product obtained possesses the following properties and advantages:

Hardening can be effected at temperatures up to 220° C. The hardened final product is highly elastic, can be punched or otherwise mechanically treated, and is indifferent to organic solvents, acids, alkalies and other strongly acting chemicals. In view of its wide range of uses the product is of special importance to electrotechnics, since it is practically unexcelled with respect to insulating power, electrical properties, small phase angle, heat retaining capacity and elasticity.

As the product can be dissolved by the known aromatic and aliphatic solvents, it can serve also for preserving and insulating all metals and alloys. For example, light metals and their alloys as well as copper, brass, etc. have been advantageously preserved through the application thereof, and it is characteristic in this respect that catalytic action by these metals during hardening could not be observed, whilst known phenol aldehyde condensates are considerably influenced by these metals already during hardening or storing with the result that in most cases the preserving layers became brittle or were knocked off from the metals.

The following examples have been found to give satisfactory results:

Example 1

100 parts o-cresol are mixed with 150 parts formaldehyde (40%) and heated with 2 parts hydrochloric acid and 1 part phosphoric acid, acting as reaction accelerator, to 90–95° C. After about 30 minutes 7 parts sodium hydroxide in diluted solution are added and for about 80–90 minutes heated up to approximately 100° C. Water separated during condensation is removed in the vacuum, whereupon 50 parts tricresyl phosphate and, say, 25–50 parts of one or more fatty

acids of the C_9 — C_{18} series, preferably from paraffin oxidation, are added and heated to 180°C . Until this temperature is reached, a violent reaction is noticeable at certain phases, which subsides, however, after about 30–60 minutes.

The resulting product can be used as plastic for pressing or as raw material for varnish, and is thermosetting.

Example 2

100 parts o-cresol are mixed with 150 parts formaldehyde (40%) and heated with 2 parts hydrochloric acid and 1 part phosphoric acid, acting as reaction accelerator, to 90 – 95°C . After about 30 minutes 7 parts sodium hydroxide in diluted solution are added and for about 80–90 minutes heated up to approximately 100°C . Water separated during condensation is removed in vacuum, whereupon 50 parts tricresyl phosphate and, say, 25–50 parts of one or more fatty acids of the C_9 — C_{18} series, preferably such from paraffin oxidation, are added and heated to 180°C . Until this temperature is reached, a violent reaction is noticeable at certain phases, which subsides, however, after about 30–60 minutes.

Then about 100 parts or more glycerides of oleic acid are added, and condensation is continued to about 190°C . After 15–20 minutes at least 5 parts polyglycols are added and also condensed and esterified at the same temperature until the condensate becomes clear.

The final product can be hardened at low and high temperatures and is particularly suited for particularly highly elastic masses. It may serve also as raw material in solid or dissolved form for varnishes.

Example 3

100 parts o-cresol are mixed with 150 parts formaldehyde (40%) and heated with 2 parts hydrochloric acid and 1 part phosphoric acid, acting as reaction accelerator, to 90 – 95°C . After about

30 minutes 7 parts sodium hydroxide in diluted solution are added and for about 80–90 minutes heated up to approximately 100°C . Water separated during condensation is removed in vacuum, whereupon 50 parts tricresyl phosphate and, say, 25–50 parts of one or more fatty acids of the C_9 — C_{18} series, preferably such from paraffin oxidation, are added and heated to 180°C . Until this temperature is reached, a violent reaction is noticeable at certain phases, which subsides, however, after about 30–60 minutes.

Then about 100 parts or more glycerides of oleic acid are added, and condensation is continued to about 190°C . After 15–20 minutes at least 5 parts polyglycols are added and also condensed and esterified at the same temperature until the condensate becomes clear.

After completion of the condensation the product is dissolved in a mixture of aliphatic and aromatic solvents and esters and mixed with metal soaps, as metallic compounds combined with naphthenic, oleic or resin acids. It is further possible of course to add these metal soaps after completion of condensation and to work them in solid form.

The final product can serve for plastics or as raw material for varnishes, is thermosetting and at low temperatures (air temperatures) polymerizable owing to catalytic action of the metal soaps.

Condensates prepared according to Examples 1 to 3, depending on their uses, can be mixed with fillers or coloring matter of inorganic or organic nature.

The uses comprise the preparation and utilization of cold and warm hardening varnishes and paints and the function as binding agent for plastics and allied industrial purposes.

The process according to the invention covers of course also the working of o-cresol in mixture with other products to be condensed, as phenol.

BERNHARD HABRASCHKA.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF ALIPHATIC DICHLORO COMPOUNDS

Hugo Kroeper, Heidelberg, Germany; vested in the Alien Property Custodian

No Drawing. Application filed August 8, 1940

The present invention relates to the production of aliphatic dichloro compounds and particularly to the preparation of 1,4-dichlorbutane and 4,4'-dichlorodibutyl ether by the interaction of aqueous hydrochloric acid and tetrahydrofurane.

The synthesis of aliphatic dihalogen compounds is well known as, for example, the preparation of 1,4-dibrombutane from 1,4-dihydroxybutane or from ethers and esters thereof and hydrobromic acid. These processes have been considered of little interest for the commercial preparation of these compounds owing to the relatively small rate of conversion.

An object of the present invention is to provide an improved process for the synthesis of 1,4-dichlorbutane and at the same time to provide a simple process for the production of 4,4'-dichlorodibutyl ether having the structural formula



According to the present invention concentrated aqueous hydrochloric acid, i. e. hydrochloric acid containing at least 20 per cent of hydrogen chloride, is allowed to act on tetrahydrofurane at temperatures exceeding 100° C, preferably in the presence of catalysts promoting the formation of alkyl halides.

In order to effect the reaction as completely as possible, it is advantageous to work under superatmospheric pressure. The pressure employed should be so high that at least part of the tetrahydrofurane is in the liquid phase, the total pressure corresponding to the vapor pressure of all constituents of the reaction mixture at the reaction temperature. By employing inert diluent gases, such as nitrogen, the pressure may be increased beyond the pressure of the reactants, for example up to 50 or 100 atmospheres or even more. The pressure may also be increased by pressing anhydrous hydrogen chloride into the reaction vessel before or during the reaction.

The reaction proceeds with fairly satisfactory conversion already at temperatures between 110 and 140° C. The most suitable temperatures are within the range of 140 to 180° C. Temperatures exceeding 180° C cause the formation of higher molecular by-products and are not practicable.

The relative proportion of the reactants can be varied although it has been found that very advantageous results are obtained when the hydrochloric acid is in excess with respect to the tetrahydrofurane. In order to obtain a preponderating amount of 1,4-dichlorbutane, at least two molecular proportions or even more, e. g. 2.5 or 3

molecular proportions, of hydrochloric acid for each molecular proportion of tetrahydrofurane should be used. The proportion of 4,4'-dichlorodibutyl ether in the reaction product may be increased by using from 1 to 2 molecular proportions of hydrochloric acid for each molecular proportion of tetrahydrofurane. Hydrochloric acid remaining unchanged and to be found in the final reaction mixture, will be found diluted by water formed in the reaction. It may be used again after having led in hydrogen chloride in order to obtain concentrated hydrochloric acid.

Catalysts may be employed in my process, though the conversion of tetrahydrofurane into 1,4-dichlorbutane and 4,4'-dichlorodibutyl ether is already satisfactory without the aid of catalysts. Suitable catalysts are those which have proved useful for promoting the formation of alkyl halides from aliphatic alcohols or olefinic hydrocarbons and hydrogen halides, such as strong, non-oxidizing mineral acids, in particular concentrated sulfuric or phosphoric acid, and also metal halides, e. g. the chlorides of iron, bismuth, mercury, zinc or calcium, or iodine or activated carbon, silica gel and the like which may be impregnated with a metal salt of the type referred to above.

In the continuous preparation of 1,4-dichlorbutane and 4,4'-dichlorodibutyl ether the use of concentrated sulfuric acid as catalyst has proved particularly useful.

A mixture of tetrahydrofurane and concentrated sulfuric acid to which concentrated hydrochloric acid has been added is heated in a closed vessel to temperatures within the range indicated above. From the resulting mixture 1,4-dichlorbutane and 4,4'-dichlorodibutyl ether are distilled off. Hydrogen chloride is then led into the remaining mixture containing sulfuric acid, water, hydrochloric acid and unchanged tetrahydrofurane, thus strengthening the concentration of the hydrochloric acid. Further tetrahydrofurane is added and the reaction is again started.

This modification of my invention may be easily operated in a cycle by using as the medium and the catalyst for the reaction a mixture of sulfuric acid and water to which tetrahydrofurane and anhydrous hydrogen chloride in appropriate proportion are continuously added at the beginning of the vessel and from which the dichloro compounds are continuously withdrawn at the end of the vessel. At the end of the vessel and after having distilled off the dichloro compounds a small portion of the aqueous sulfuric acid is replaced by concentrated sulfuric acid in order to

maintain the concentration of the sulfuric acid present in the reaction.

When carrying out the process according to my invention with the aid of sulfuric acid, it is even possible to work at normal pressure, for example by allowing a mixture of tetrahydrofurane and aqueous sulfuric acid to flow through the vessel in counter-current to gaseous hydrogen chloride.

The following examples will illustrate methods of practicing the invention although the invention is not limited to the examples. The parts are by weight.

Example 1

A mixture of 120 parts of tetrahydrofurane, 164 parts of concentrated sulfuric acid and 440 parts of 38 per cent hydrochloric acid is heated under a pressure of 25 atmospheres to 150° C. in a vessel lined with lead for 4 hours. By distilling the reaction product under reduced pressure there are obtained 157 parts of 1,4-dichlorbutane and 20 parts of 4,4'-dichlordibutyl ether.

When heating a mixture of 120 parts of tetrahydrofurane, 164 parts of concentrated sulfuric acid and 350 parts of 33 per cent hydrochloric acid to 170° C. under a pressure of 15 atmospheres for 4 hours, there are formed 153 parts of 1,4-dichlorbutane and 22.5 parts of 4,4'-dichlordibutyl ether.

Example 2

150 parts of hydrogen chloride are led into a mixture of 360 parts of tetrahydrofurane, 60 parts

of concentrated sulfuric acid and 630 parts of 38 per cent hydrochloric acid. The whole is heated in a pressure-tight vessel to 170° C. under a pressure of about 110 atmospheres for 4 hours. 354 parts of 1,4-dichlorbutane and 61 parts of 4,4'-dichlordibutyl ether are thus obtained.

Example 3

A mixture of 180 parts of tetrahydrofurane, 1000 parts of 38 per cent hydrochloric acid and 2.4 parts of bismuth trichloride are heated to 160° C. under a pressure of 30 atmospheres for 4 hours. 210 parts of 1,4-dichlorbutane and 20 parts of 4,4'-dichlordibutyl ether are thus obtained.

Example 4

160 parts of anhydrous hydrogen chloride are led into a mixture of 153 parts of 94 per cent tetrahydrofurane with 400 parts of 50 per cent sulfuric acid while cooling. The whole is heated in a pressure-tight vessel to 160° C. under 20 atmospheres pressure for 3 hours. The resulting mixture forms two layers, the aqueous layer consisting of sulfuric acid, water, hydrochloric acid and small amounts of tetrahydrofurane, the non-aqueous layer consisting of from 88 to 90 per cent of 1,4-dichlorbutane and from 10 to 12 per cent of 4,4'-dichlordibutyl ether. About 90 per cent of the tetrahydrofurane are thus converted. The aqueous layer may again be used for a new batch.

HUGO KROEPER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF POLYMERIZATION PRODUCTS

Curt Schuster, Rudolf Sauerbier, and Hans
Fikentscher, Ludwigshafen-on-Rhine, Ger-
many; vested in the Alien Property Custodian

No Drawing. Application filed August 10, 1940

The present invention relates to a process for the manufacture of polymerization products.

We have found that valuable polymerization products are obtained by polymerizing N-vinyl lactams, either alone or in admixture with other polymerizable compounds containing one or more omega-methylene groups in the presence of oxygen or substances supplying oxygen.

Suitable N-vinyl lactams are, for example, N-vinyl-alpha-pyrrolidone, N-vinyl-alpha-piperidone, N-vinyl-hexahydrophthalimidine and N-vinyl-caprolactam.

Among compounds containing an omega-methylene group and which are suitable for being interpolymerized with N-vinyl lactams there may be mentioned for example acrylic acid and its derivatives and homologues, such as acrylic esters, acrylic nitrile and methacrylic esters, unsaturated ketones, such as vinyl methyl ketone and vinyl chloride.

Among substances supplying oxygen there may be mentioned hydrogen peroxide, persulphates, peracetic acid and inorganic and organic peroxides. The polymerization may be carried out in a block, i. e. in a coherent mass and in the absence of a diluent or in the presence of diluents or solvents, as for example water or alcohols. It is preferable to work at a moderately elevated temperature, especially at from 40 to 150° C., in an open or closed vessel, with or without reflux cooling. By shaking or stirring the reaction may be accelerated in many cases.

The products obtained are from viscous to horny or glass-like, sometimes also brittle materials possessing a high softening point. They swell and dissolve partly in water, partly only in certain organic solvents. They form solutions of high viscosity possessing good sticking power which properties render them valuable for a variety of technical applications, as for example as sizes and adhesives, as protective colloids or emulsifying or thickening agents, as well as binders, as for example for lacquers. When used for producing interpolymerization products, the N-vinyl lactams improve the resistance of the products to solvents, especially to benzene, and raise the softening point thereof.

The following examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said examples. The parts are by weight.

Example 1

50 parts of N-vinyl-alpha-pyrrolidone and 1 part of 3 per cent. hydrogen peroxide are heated

at 110° C. for 3 hours in a pressure-tight vessel, a solid colorless polymerization product being formed in a quantitative yield. In the same manner polymerization products of N-vinyl caprolactam and N-vinyl hexahydrophthalimidine can be prepared.

Example 2

50 parts of N-vinyl-alpha-pyrrolidone and 1 part of potassium persulphate (or 0.5 part of 3 per cent. hydrogen peroxide and 0.5 part of potassium persulphate) are heated under the same conditions as in Example 1, a viscous brown polymerizate being formed in a good yield.

Example 3

50 parts of N-vinyl-alpha-pyrrolidone, 1 part of water and 0.1 part of benzoyl peroxide are heated at 100° C. for 8 hours in a pressure-tight vessel, a yellow viscous polymerizate being obtained in a good yield.

Example 4

50 parts of N-vinyl-alpha-pyrrolidone and 1 part of sodium peroxide (or 0.5 part of sodium peroxide and 0.5 part of 3 per cent. hydrogen peroxide) are heated at 110° C. for 6 hours in a strong-walled vessel, an amorphous pulverulent polymerization product being obtained.

Example 5

50 parts of N-vinyl-alpha-pyrrolidone, 100 parts of ethanol, 5 parts of 3 per cent. hydrogen peroxide and 0.5 part of benzoyl peroxide are heated to boiling under reflux cooling for 5 hours. After removing the ethanol by distillation, a viscous brown polymerization product remains.

Example 6

50 parts of N-vinyl-alpha-pyrrolidone, 100 parts of ethanol, 5 parts of water and 2.5 parts of 3 per cent. hydrogen peroxide are heated under the conditions specified in Example 5. After evaporating the solvent a solid, pale yellow polymerization product is obtained in a quantitative yield.

Example 7

A mixture of 70 parts of acrylic acid (100 per cent. strength) in the form of a 73 per cent. solution, 30 parts of N-vinyl-alpha-pyrrolidone, 30 parts of sodium carbonate, 200 parts of water and 0.2 part of potassium persulphate is heated to 50 to 60° C. while stirring. Polymerization takes place with evolution of heat. It is finished after some hours. The polymerization product obtained is treated with steam and thus freed

from slight residual amounts of monomers. An interpolymerization product is thus obtained in the form of a highly viscous clear solution, which is suitable as adhesive.

Example 8

A mixture of 55 parts of acrylic acid (100 per cent. strength), 45 parts of N-vinyl-alpha-pyrrolidone and 100 parts of water is heated to 85 to 90° C, whereupon 7.5 parts of 30 per cent. hydrogen peroxide are added. The whole is then stirred at between 85 and 90° C for 3 hours, a viscous, water-clear solution of the interpolymerization product formed being obtained which by treatment with steam may be freed from any residual amounts of monomers, if desired.

Example 9

A mixture of 35 parts of acrylic acid (100 per cent. strength), 15 parts of N-vinyl-alpha-pyrrolidone, 20 parts of sodium carbonate, 50 parts of vinyl chloride, 300 parts of water and 1 part of sodium persulphate is shaken in a shaking bomb for 40 hours at 40° C. The interpolymerization product formed is precipitated by means of dilute sulphuric acid. It may be pressed into plates at high temperature. The product is soluble in benzine and benzene, while it swells in acetone.

CURT SCHUSTER.
RUDOLF SAUERBIER.
HANS FIKENTSCHER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR IMPROVING THE PROPERTIES OF RUBBER LATEX

Johan Hubert Egbert Hessels, Klein Soengei-Karang, Galang Sumatra, Netherlands East Indies; vested in the Alien Property Custodian

No Drawing. Application filed August 12, 1940

The invention is concerned with improving the properties of rubber latex.

It is based on decomposing the proteins present in the latex under special conditions. It is already known that rubber with a minimum protein content can be obtained by decomposing the proteins present in the latex through heating with alkali which, at the same time, keeps the latex from coagulating during the heating for which purpose quantities of 0.5 to 3% calculated on the weight of the latex are prescribed. After such treatment the latex is coagulated in the ordinary way.

But according to the new process, which aims at the preparation of an improved rubber latex or rubber cream, much smaller quantities of lye (alkali) are used than in the process described above, namely by not dosing them for a complete decomposition of its proteins, but by using only just the quantity that is necessary to keep the latex liquid during subsequent heating. This heating may, it is true, take place at different temperatures, which in turn affect the duration of the heating, but in order to give a concrete example for practical application, heating for about an hour at a temperature of about 135° C. is presumed for present purposes. If the heating is obtained by aid of saturated steam, which is the simplest way, a steam pressure of 3 atmospheres is sufficient, so that no great demands are made as regards apparatus.

When heating under these conditions, it appears that an addition of only 0.10% of alkali, calculated as sodium hydroxide (NaOH) in relation to the weight of the latex, is sufficient to keep normal fresh latex—that is latex containing about 35–40% of solid substance—from coagulating. It will be understood, however, that this small quantity is not capable of decomposing the proteins sufficiently, but it has now been found that it is still possible to obtain a sufficient decomposition of the proteins if, in addition to the lye, a small quantity of a stabilizer and/or an emulgator is added to the latex which is then heated.

Emulgators are understood to be substances that promote the formation of emulsions and the like; under stabilizers are included substances which protect the stability of such systems against mechanical, chemical, calorific and other influences. It is often impossible to make a sharp distinction between these two classes of substances for many substances are to be reckoned among both classes. As examples of such substances may be mentioned: soaps, fatty acids, sulfonated fatty acids and their derivatives, as described in the French Patent Letter 727 202.

The minimum quantity of alkali is somewhat dependent on the concentration of the latex. E. g. for a latex with a rubber content of 30%,

even 0.06 to 0.08% of sodium-hydroxide is sufficient.

If it is desired to heat at a higher temperature, it should be taken into account that there is then greater danger of the latex's coagulating, so that more alkali will have to be used to prevent such coagulation. So, when heating to about 150° C., it will be necessary to use a quantity of 0.12 to 0.15% lye, calculated as NaOH with regard to the weight of the latex.

A latex, prepared as mentioned above, now shows the following improvements in its properties:

1. It creams more quickly.
2. In the process of creaming it yields a higher cream percentage than does a latex not so treated creaming under the same conditions.
3. It remains clear when stored in iron vessels, and
4. It requires much less ammonia for conservation.

These improvements will be dealt with separately hereunder.

Ad 1 and 2. In creaming latex, often the difficulty is encountered that unless the latex has been specially treated beforehand, a cream of a sufficiently high percentage is not obtained.

In this regard, latex of young plantations and of diverse clones present special difficulty.

Improvement in creaming can be obtained e. g. by removing some of the proteins from the latex e. g. by previous coagulation, or by aid of absorbing agents, or by clarifying, or by speeding up the creaming by addition of soaps, or by dehydration of the dispersed rubber particles, or by other means.

Notwithstanding such preparatory treatment of the latex, the latex mixture should be allowed to stand for at least 2–3 days in order to obtain from a complete creaming a cream of sufficiently high rubber content of 60–63%. This long creaming time requires a fairly great quantity of conserving agents and a large tank capacity.

It appears that from treatment beforehand as prescribed by the invention, the latex obtains a surprisingly good creaming capacity so that, after mixing the latex with creaming agents in an ordinary creaming vessel, about 0.9 of the serum is separated in as short a time as 1–2 hours.

Ad 3. One disadvantage of conserved latex is its tendency to become gray in colour when influenced by traces of iron salts due to the formation of iron sulphide.

When casking and storing latex in iron vessels and tanks, special precautions must always be taken to prevent the latex being spoiled by the iron, whereby an inferior product would be obtained.

Such decolorization can be prevented by pro-

viding the interior of tanks, pipes and drums with a protecting layer which has to be frequently renewed, which in practice involves much cost and labor.

Latex previously treated according to the invention and the cream obtained therefrom appear to be much less susceptible to iron discolorization than untreated latex. Without more ado the cream can be casked in iron vessels without discoloration occurring. Under these circumstances the previously treated latex itself has only a slight tendency to discolour in contrast with ordinary latex and cream-latex, both of which discolour very much in iron vessels.

Ad 4. In consequence of the great susceptibility of latex to infection by micro-organisms, up to now satisfactory conservation has only been obtained by adding comparatively large amounts of preservatives.

Although several substances have been suggested as preservatives for latex, in up to date practice ammonia has proved to be the most suitable and has consequently been most used.

A durable conservation of latex by ammonia not only makes it much more expensive, but under certain circumstances the rather high concentration of conserving agent proves to be undesirable for use of the latex in manufacture.

As a cheap preservative strong alkali would come under consideration if proper doses of this substance were not to have unfavourable effects on the properties of rubber and therefore were only to be applicable in special cases.

Also during the concentration of latex by creaming, centrifuging, or dialysing, a fairly large dose of conserving agent must be added to the latex to prevent vitiation during treatment. But a large proportion of the preservative is again lost in the serum (the under-latex), so that in such processes the costs of conservation become extra high.

A latex, previously treated according to the invention, and having a very low percentage of alkali, namely a pH of about 9 or somewhat lower, keeps for an indefinite period if it is casked in sterilized drums.

Even if not sterile, such latex appears to be much less susceptible to infection than ordinary latex, so that for a durable conservation an addition of 0.20–0.25% ammonia is sufficient, while the usual quantity for ordinary latex amounts to about 0.7%.

The cream too, which is easily obtained from latex that has been treated according to the invention by the addition of a creaming agent and which, according to circumstances, contains 60–64% dry substance after a creaming period of 12–15 hours, requires only a small quantity of about 0.15% ammonia for protection against infection.

After the conservation, the cream may still be allowed to stand for a short time e. g. for a week, whereby an aftercreaming takes place in the cream, whereafter after separation from the serum the cream contains up to 66–67% dry substance.

As already mentioned in the beginning, the treatment of latex with lye has often been described, but then the conditions prescribed were quite different.

In processes aiming at the complete decomposition of proteins by heating with lye, high lye concentrations are used, varying between 0.5 and 3% sodium-hydroxide calculated on the latex.

But this high dose of alkali and the high ash content of the rubber obtained from such latex by evaporation have undesirable effects on products manufactured therefrom, such as a pronounced tendency to absorb water, an insufficient isolation capacity, and bad durability. Such latex is, therefore, generally not in demand by manufacturers of rubbergoods.

On the other hand, during dehydration of the latex, when it is heated with a small quantity of ammonia or lye, the exact temperature and time are not so chosen that there can be said to have been a decomposition of proteins, so that such previous treatment does not improve the properties of the latex, as is the case according to the present process.

The process is elucidated in more detail by the following examples:

Example I.—45 cm³ of 10 n-sodium-hydroxide were added to 15 liters of latex with a 36% total solids (T. S.) content, after which 30 grams of oleic acid were stirred into the latex. The latex was heated at 135° C. in an autoclave for 60 minutes.

The improvement of the latex was shown by diluting a part of the latex to 5%, and coagulating the rubber, which had a nitrogen content of 0.03% and an ash content of 0.10%, both calculated on the dry rubber.

One portion of this latex was durably conserved by addition of 0.25% ammonia, for after 4 months the alkalinity had not perceptibly decreased.

Another portion of this latex was durably conserved by using 0.2% pentachloric phenolsodium instead of ammonia.

After keeping the latex conserved with ammonia for 2 months in an unlacquered iron drum, the latex was only discoloured to a light gray equivalent to colour No. 2–3 on Davey's colour-card (India Rubber Journal, 1938, pg 321). Under the same circumstances normal ammonia latex became dark gray equivalent to colour No. 7 on the same card.

Example II.—40 cm³ of 10 n-sodium-hydroxide and 30 grams of oleic acid were added to 15 liters of latex with 33% total solids (T. S.).

The latex was heated at 135° C. in an autoclave for 60 minutes.

After cooling down to about 80° C., 1.5 liter of a 1% Ilesmann meal-solution, a creaming agent, was added, whereupon the latex was allowed to cream in an isolated creaming vessel without any further addition of conserving agent.

After a creaming period of 15 hours, the cream-layer had a dry-substance content of 62.6%. The rubber, obtained by drying up the cream, contained 0.19% nitrogen and 0.75% ash, both calculated on the total solids (T. S.).

After 4 weeks, the waterabsorption of the dried rubber-film in an atmosphere of 90% relative humidity amounted to 3.7% as against 4.1% for a similar sample of centrifugated latex.

One part of that cream was durably conserved by the addition of 0.15% ammonia.

Another portion was durably conserved with 0.2% pentachloric phenolsodium, without adding any ammonia.

After keeping the cream for 2 months in an unlacquered iron drum, the colour of the latex appeared almost unchanged, while a creamed concentrate prepared in the normal way was greatly discoloured.

JOHAN HUBERT EGBERT HESSELS.

ALIEN PROPERTY CUSTODIAN

THERAPEUTICALLY ACTIVE TETRAHYDRO-ISOQUINOLINE COMPOUNDS AND PROCESSES FOR THEIR PRODUCTION

Fritz Kütz, Francfort-on-the-Main, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed August 12, 1940

The invention concerns new, therapeutically active tetrahydroisoquinoline compounds and processes for their production.

It has been found that tetrahydroisoquinoline compounds which are substituted in the hydrogenated pyridine nucleus by an aliphatic radical, substituted by a phenyl radical and only in one benzene ring by at least 2 acyloxy (esterified hydroxy) groups, have an analgesic effect. As aliphatic radicals, which are substituted by phenyl, aralkyl or aralkenyl rests may be used. The hydroxy groups may be esterified by formic acid, acetic acid, propionic acid, butyric acid or other organic acids. It is advantageous to employ acetylated compounds. The compounds may, however, carry further substituents, for example alkyl or alkenyl groups, in various positions of the molecule; for example they may be substituted in the hydrogenated pyridine ring or in one or both of the benzene nuclei or in several nuclei or in the aliphatic intermediate chain by methyl, ethyl, propyl, butyl, vinyl, propenyl, butenyl or the like rests. Finally the compounds may be substituted at the benzene nucleus, which is free from acyloxy groups, by one free hydroxy group and/or one or more etherified hydroxy groups, for example alkoxy or alkylendioxy groups. The presence of more than one hydroxy group in the second benzene nucleus annuls the analgesic effect.

The new compounds may be prepared according to various methods. Tetrahydroisoquinoline compounds, which are substituted at the nitrogen by an aralkyl or aralkenyl rest are prepared by adding on to the nitrogen atom of an isoquinoline, dihydroisoquinoline or tetrahydroisoquinoline the desired aralkyl or aralkenyl rest. This addition may be effected by letting act derivatives of aralkyl or aralkenyl alcohols, for example halogenides, benzenes or toluene sulfonic acid esters or aldehydes or ketones (according to Leuckart-Wallach) on the starting compounds, one of these reaction partners containing at least 2 acyloxy compounds.

Starting from isoquinolines or dihydroisoquinolines quaternary salts are obtained during the addition of aralkyl or aralkenyl groups, which must be converted into the corresponding tetrahydroisoquinoline compounds by hydrogenation. Hydrogenation may be carried into effect according to the desired product by only hydrogenating the double bonds of the pyridine ring or both the double bonds of the aralkenyl substituents and the pyridine ring. Hydrogenation may be carried out

catalytically, or, in the case of partial reduction, with metals, if desired in the presence of acids.

The compounds to be converted may be substituted besides by acyloxy groups by alkyl or alkenyl rests in any desired position. Furthermore the compound involved in reaction, which does not contain any acyloxy groups, may be substituted by one free hydroxy group and/or one or more etherified hydroxy groups, such as alkylendioxy groups.

On the other hand tetrahydroisoquinoline compounds, which are substituted at one of the carbon atoms of the hydrogenated pyridine ring by an aralkyl or aralkenyl rest and in one of the two benzene rings by at least two acyloxy groups may be prepared by hydrogenation of corresponding, not completely hydrogenated compounds. As starting material for this hydrogenation non hydrogenated or dihydrogenated isoquinoline compounds, substituted at one of the carbon atoms of the pyridine ring by an aralkyl or aralkenyl group or their quaternary ammonium salts or tetrahydrogenated isoquinoline compounds, which are substituted at one of the carbon atoms of the hydrogenated pyridine ring by an aralkenyl rest may be employed. All of these compounds must be substituted at the benzene nucleus by at least 2 acyloxy groups. Moreover they may contain further substituents, for example alkyl or alkenyl groups, in various positions of the molecule and may be substituted in the second benzene nucleus, which is free from acyloxy groups, by one free hydroxy group and/or its functional derivatives, such as alkylendioxy groups.

For the preparation of tetrahydroisoquinoline compounds, which are substituted by aralkyl, one may proceed from various starting materials. Non hydrogenated or dihydrogenated isoquinoline compounds, which are substituted at one of the carbon atoms of the pyridine ring by aralkyl, which contain at least 2 acyloxy groups in one benzene nucleus and are, if desired, further substituted, or their quaternary ammonium salts may be hydrogenated in a manner known per se, whereby the double bonds of the pyridine ring are converted into single bonds. This hydrogenation either may be carried into effect by help of metals, for example zinc dust, if desired in the presence of the acid, by which the hydroxy groups are acylated, or catalytically, for example by help of platinum or palladium catalysts, such as platinum black, platinum oxide, palladium, palladium black, palladium charcoal. One may, however, start from the corresponding, non hydrogenated

isoquinoline compounds or dihydroisoquinoline compounds, which are substituted by aralkenyl, or their quaternary ammonium salts, and hydrogenate these starting materials catalytically, for example in the presence of platinum or palladium catalysts in such a manner that the double bonds of the pyridine ring, as well as the double bonds of the aralkenyl rest are converted into single bonds. Finally one may proceed from the corresponding tetrahydroisoquinoline compounds, which are substituted by aralkenyl and hydrogenate also these catalytically, the aralkenyl substituents being converted into aralkyl substituents.

If, on the other hand, tetrahydroisoquinoline compounds, substituted by an aralkenyl rest of the kind described as above, are to be produced, nonhydrogenated or dihydrogenated isoquinoline compounds, which are substituted at one of the carbon atoms of the pyridine ring by an aralkenyl rest and which contain at least 2 acyloxy groups in the benzene nucleus and which are, if desired, furthermore substituted, or their quaternary ammonium salts are employed as starting materials and are hydrogenated with metals, if desired in the presence of the acid, with which the hydroxy groups are acylated, in such manner that only the double bonds of the pyridine ring are converted into single bonds, the double bonds of the aralkenyl substituents, however, are preserved.

The starting material for these hydrogenating processes may, for example, be obtained by condensation of, if desired, correspondingly substituted 1-methyl isoquinolines or 1-methyl-3,4-dihydroisoquinolines with, if desired, correspondingly substituted aromatic aldehydes or, by the Bischler-Napieralsky synthesis, from correspondingly substituted β -phenylethylamines.

Finally the tetrahydroisoquinoline compounds according to the invention, which are substituted by an aralkyl or aralkenyl rest and at least 2 acyloxy groups, may be produced independently of their carrying the aralkyl or aralkenyl substituents at the nitrogen or at one carbon atom of the hydrogenated pyridine ring, by esterifying corresponding compounds with free hydroxy groups.

One may, however, for this production start from compounds, which, besides being substituted by an aralkyl or aralkenyl rest in the hydrogenated pyridine ring and free hydroxy groups in one benzene nucleus are substituted by further substituents, for example alkyl and alkenyl groups in various positions of the molecule and/or in the second benzene nucleus by one free hydroxy group and/or its functional derivatives.

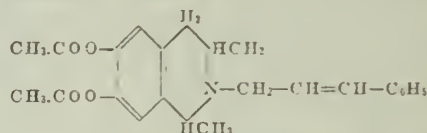
Esterification of the starting materials may, regardless whether secondary or tertiary tetrahydroisoquinolines (in respect of the amino group) are employed, be effected by heating with acid anhydrides or chlorides to temperatures of 80–90° C. and above, if desired under dilution with the acid, with which the hydroxy groups are to be acetylated. In the case of starting from secondary amines these must be employed in the form of their salts, in order to guarantee an acetylation only or mainly at the oxygen, temperatures not exceeding 90° C. being employed. Starting from tertiary amines the free bases and boiling temperatures may be employed. On the other hand in this case the treatment with acid anhydride or chloride may be carried out in the presence of tertiary bases, for example pyridine, and even in the cold.

In this manner acetoxy, propionyloxy and butyryloxy compounds, as well as compounds esterified with higher organic acids may be produced. In addition acetoxy compounds may be obtained by treatment of the starting products with ketene, while the formyl oxy compounds may be produced by boiling of the starting material with formic acid.

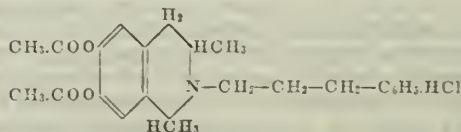
Examples

(1.) 7.1 grs. of hydrobromide of 1,3-dimethyl-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline, melting point 238–240° C. are solved in water, and mixed with potash. The free base is extracted with ether. 1.9 grs. of freshly produced γ -phenyl-allylbromide are added to the well dried ether solution. This mixture is heated to boiling under reflux for 5 hours. After evaporation of the ether the residue is heated to 100° C. for 30 minutes. This residue is again solved in ether, the hydrobromide of the initial base filtered with suction and the 1,3-dimethyl-2-(γ -phenylallyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline precipitated from the ether solution by ethereal hydrobromic acid. The hydrobromide precipitates amorphous and is solved in water. The solution is rendered alkaline with potash under cooling with ice. The base is extracted with ether and the ether residue distilled off in high vacuo. After first runnings of unchanged starting material 1.8 grs. of 1,3-dimethyl-2-(γ -phenylallyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline are distilled at 170–180° C. bath temperature as a colourless, noncrystallizing resin, under a pressure of 0.004 mm. Hydrochloride and hydrobromide are also amorphous.

Formula:



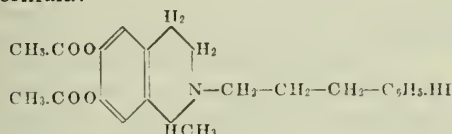
(2.) 2.2 grs. of 1,3-dimethyl-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline, produced by acetylation of the hydrobromide of 1,3-dimethyl-6,7-dioxy-1,2,3,4-tetrahydroisoquinoline with acetic acid anhydride in glacial acetic acid, or by catalytic hydrogenation of the hydrobromide of 1,3-dimethyl-6,7-diacetoxy-3,4-dihydroisoquinoline in glacial acetic acid, solving of the hydrobromide (melting point 240–242° C.) in water, rendering alkaline and extracting with ether, are heated to 60° C. for 6 hours, after 1.0 grs. of γ -phenyl-propyl iodide have been added, under careful exclusion of moisture. After cooling the hydroiodide of the starting base is precipitated with ether. After first runnings the obtained base, which is solved in ether, is distilled off in high vacuo under 0.01 mm. pressure at 190–220° C. bath temperature. The base is solved in ether, filtrated and the 1,3-dimethyl-2-(γ -phenylpropyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride is precipitated with hydrochloric acid in ether and melts at 154–156° C. after re-crystallization from methanol under the addition of absolute ether.



(3.) 2.6 grs. of 1-methyl-6,7-diacetoxy-3,4-dihydroisoquinoline, produced by acetylation of 1-

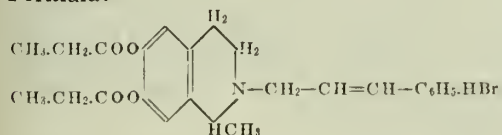
methyl-6,7-dioxy-3,4-dihydroisoquinoline-hydrobromide with acetic acid anhydride at 100° C., solving in water, precipitating with icy cold, saturated potassium carbonate solution and extraction with ether, are heated, together with 3,4 grs. of γ -phenol-propyliodide to 70° C. for 1/2 hour. The mixture is triturated with ether and the obtained 1-methyl-2-(γ -phenylpropyl)-6,7-diacetoxy-3,4-dihydroisoquinolinium-iodide is re-crystallized from absolute alcohol. Hereon the quaternary salt, which is melting at 194–196° C. is reduced by 2 hours' boiling with zinc dust in glacial acetic acid. After the hot zinc dust is filtered off with suction one precipitates the filtrate with ether, solves the precipitate in methanol and pours the solution into icy cold diluted ammonia. The precipitating base is extracted with ether. The ethereal solution is washed with icy cold, diluted soda lye and water, dried and evaporated. The residue, i. e. 1-methyl-2-(γ -phenylpropyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline distills in high vacuo of 0.01 mm pressure at 180–185° C. bath temperatures.

Formula:



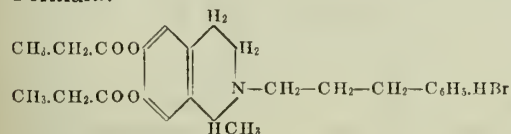
(4.) A mixture of 0.6 grs. of 1-methyl-6,7-dipropionyloxy-3,4-dihydroisoquinoline and 0.8 grs. of γ -phenylallylbromide are heated to 60° C. for 10 minutes. The mixture is triturated with ether and filtered with suction. The obtained 1-methyl-2-(γ -phenylallyl)-6,7-dipropionyloxy-3,4-dihydroisoquinolinium-bromide is solved in the 10-fold amount of propionic acid and reduced by 3 hours' boiling with 1 g of zinc dust at 100° C. The process is completed according to example 3. The obtained 1-methyl-2-(γ -phenylallyl)-6,7-dipropionyloxy-1,2,3,4-tetrahydroisoquinoline is distilled off in high vacuo at 195–200° C. under a pressure of 0.01 mm.

Formula:



(5.) 1 gr. of 1-methyl-2-(γ -phenylallyl)-6,7-dipropionyloxy-3,4-dihydroisoquinolinium-bromide, produced according to example 4, are shaken in 10 ccs. of propionic acid with a palladium-bariumsulfate-catalyst and hydrogen, a greater amount of hydrogen being added than was calculated for two molecules. The solution is filtered off from the catalyst and evaporated in vacuo. The residue is solved in water and the obtained base precipitated with soda. The obtained compound is extracted with ether. After first runnings the 1-methyl-2-(γ -phenylpropyl)-6,7-dipropionyloxy-1,2,3,4-tetrahydroisoquinoline is obtained and distilled off in high vacuo at 190–200° C. bath temperature.

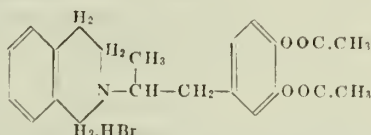
Formula:



(6.) 1 g of 2-[α -methyl- β -(3',4'-diacetoxy-phenyl)-ethyl]-isoquinolinium-bromide, produc-

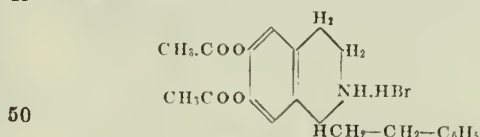
ed by letting act homophthalaldehyde on α -methyl- β -(3,4-diacetoxy-phenyl)-ethyl-amine-hydrobromide, melting point 150–152° C., are heated to boiling in 5 ccs of glacial acetic acid with 1 g of zinc dust for 2 hours at the reflux condenser. The solution, which has decolorized, is filtered off from the hot remaining zinc dust. The filtrate is precipitated with ether and the precipitate solved in a little methanol and pourn into icy cold, diluted ammonia in excess. The precipitating base is extracted with ether, the ethereal solution washed with icy cold, diluted sodium hydroxide dried and evaporated. The residue, i. e. the 2-[α -methyl- β -(3',4'-diacetoxy-phenyl)-ethyl]-1,2,3,4-tetrahydroisoquinoline is distilled off in high vacuo under 0.01 mm pressure at temperatures ranging between 180 and 185° C. bath temperature.

Formula:



(7.) 3 2.0 grs. of 1-(β -phenylethyl)-6,7-diacetoxy-3,4-dihydroisoquinoline hydrobromide, melting point 142–144° C., which have been re-crystallized from a mixture consisting of absolute ether and acetic ester, are shaken in 30 ccs. of glacial acetic acid with platinum from 0.1 g of platinum oxyde and with hydrogen. After an amount of hydrogen has been absorbed, which corresponds to 1 mole hydrogen, hydrogenation comes to a standstill. The obtained product is filtered off from the catalyst and evaporated in vacuo. The obtained 1-(β -phenylethyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline-hydrobromide is re-crystallized from absolute ether. The hydrobromide melts at 180–181° C. From the aqueous solution of the hydrobromide the sodium hydrochloride solution precipitates the free base, which is unsoluble in soda lye and may be solved therein only slowly under saponification.

Formula:

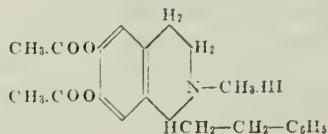


(8.) 0.9 grs. of 1-(β -phenylvinyl)-6,7-diacetoxy-3,4-dihydroisoquinoline-hydrobromide, melting point 190–191° C. are shaken in 30 ccs. of glacial acetic acid with platinum from 0.06 grs. of platinum oxyde in a hydrogen atmosphere. In the course of one hour an amount of hydrogen, corresponding to 2 mole hydrogen is taken up. After filtering off the catalyst one works up the filtrate according to example 7. The 1-(β -phenylethyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline-hydrobromide, which has been described in example 7, is obtained.

(9.) 2 grs. of 1-(β -phenylethyl)-2-methyl-6,7-diacetoxy-3,4-dihydroisoquinolinium-iodide, melting point 175–176° C., are heated to boiling for 2 hours in 10 ccs. of glacial acetic acid with 1 g of zinc dust. The solution, which was at first was yellow, has lost all colour. The hot zinc dust is filtered off with suction. The reaction product is precipitated with ether, the precipitate solved in a little methanol, pourn into icy cold diluted ammonia in excess and extracted with a considerable amount of ether. After evaporation of the ether, which has been washed with diluted

soda lye and water and then been well dried the remaining 1-(β -phenylethyl)-2-methyl-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline is distilled over in high vacuum of 0.05 mm pressure at 210–220° C. bath temperature. By precipitation of its ethereal solution with hydrochloric acid in ether the 1-(β -phenylethyl)-2-methyl-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline is converted into hydrochloride, which is easily soluble in water.

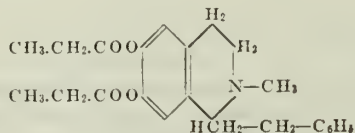
Formula:



(10.) 1.0 gr. of 1-(β -phenylethyl)-2-methyl-6,7-diacetoxy-3,4-dihydroisoquinolinium-iodide is shaken in 10 ccs. of glacial acetic acid and platinum from 0.2 grs. platinum oxide under hydrogen. After an amount of hydrogen has been absorbed, which corresponds to 1 mole, hydrogenation comes to a stand-still; the originally yellow solution has lost all colour. The solution is filtered off from the catalyst, evaporated in vacuo; the residue is solved in water and the free base precipitates with soda solution. The precipitate is extracted with ether. The ether is washed with diluted icy cold sodium hydroxide and water and then dried and evaporated. The remaining 1-(β -phenylethyl)-2-methyl-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline has already been described in example 9.

(11.) 1.0 g of 1-(β -phenylvinyl)-2-methyl-6,7-dipropionyloxy-1,2,3,4-tetrahydroisoquinoline is shaken in 10 ccs. of glacial acetic acid with platinum from 1 g of platinum oxide and with hydrogen. After an amount has been absorbed, which corresponds to 1 mole of hydrogen, hydrogenation comes to a stand-still. The hydrogenated produce is filtered from the catalyst and worked up according to example 10. The obtained 1-(β -phenylethyl)-2-methyl-6,7-dipropionyloxy-1,2,3,4-tetrahydroisoquinoline is distilled off in high vacuo under 0.05 mm pressure at 220–230° C. bath temperature.

Formula:



(12.) 0.5 grs. of 1,3-dimethyl-2-(γ -phenylpropyl)-6,7-dioxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride and 3 ccs of acetic acid anhydride are heated to boiling for one hour. Hereafter the remaining acetic acid anhydride is evaporated in vacuo and the residue is dried over night in a vacuum exsiccator charged with caustic potash. The residue is extracted with acetic ester under addition of such an amount of absolute alcohol that a lasting turbidity is observed. By trituration, preferably with vaccination crystals, complete crystallization is effected within a few minutes. 1,3-dimethyl-2-(γ -phenylpropyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride is obtained, which has already been described in example 2.

(13.) 2.0 grs. of 1,3-dimethyl-2-(γ -phenylpropyl)-6,7-dioxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride are left standing for 24 hours at

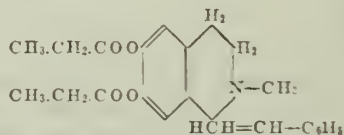
room temperature with 6 ccs. of a mixture from equal parts of acetic acid anhydride and pyridine under exclusion of moisture. After precipitation with absolute alcohol, filtration with suction and crystallization from absolute methanol under the addition of ether, 1,3-dimethyl-2-(γ -phenylpropyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride is obtained, which has already been described in example 2.

(14.) 1.5 grs. of 1,3-dimethyl-2-(γ -phenylallyl)-6,7-dioxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride and 8 ccs. of acetic acid anhydride are heated to 100° C. for 2 hours. The remaining acetic acid anhydride is distilled off in vacuo, the residue solved in water. The solution is acid extracted with ether and precipitated by the addition of soda solution. The obtained 1,3-dimethyl-2-(γ -phenylallyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline has already been described in example 1.

(15.) 1 g of 1-(β -phenylethyl)-6,7-dioxy-1,2,3,4-tetrahydroisoquinoline-hydrobromide, melting point 196–197° C. and a mixture of 3 grs. of acetic acid anhydride and 3 grs. of glacial acetic acid are heated to 85–90° C. for 2 hours, the substance dissolving in the course of 15 minutes. The solution is precipitated with absolute ether and filtered with suction. The filtrate is washed thoroughly with ether. The obtained 1-(β -phenylethyl)-6,7-diacetoxy-1,2,3,4-tetrahydroisoquinoline-hydrobromide described in example 7 is re-crystallized from absolute alcohol.

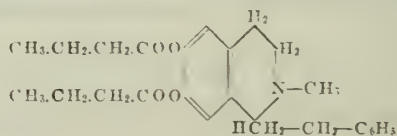
(16.) 1 g of 1-(β -phenylvinyl)-2-methyl-6,7-dioxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride, which, re-crystallized from alcohol, melts at 128° C. with foaming, and 3 grs. of propionic acid anhydride are heated to 80–85° C. for 3 hours. The mixture is poured into absolute ether. The hydrochloride of the dipropionyl compound is filtered with suction. The filtrate is solved in water and extracted with ether for purification. The obtained base is liberated by the addition of soda solution and is taken up in ether. The ether solution is washed shortly with icy cold diluted sodium hydroxide and dried. The residue of ether is dried under high vacuum. The 1-(β -phenylvinyl)-2-methyl-6,7-dipropionyloxy-1,2,3,4-tetrahydroisoquinoline is distilled off in vacuum under 0.05 mm pressure at bath temperatures ranging between 220 and 230° C.

Formula:



(17.) 1 g of 1-(β -phenylethyl)-2-methyl-6,7-dioxy-1,2,3,4-tetrahydroisoquinoline-hydrochloride is treated with butyric acid anhydride and worked up according to example 16. The obtained 1-(β -phenylethyl)-2-methyl-6,7-dibutyryloxy-1,2,3,4-tetrahydroisoquinoline is distilled in high vacuo of 0.05 mm pressure at 230–240° C. bath temperature.

Formula:



FRITZ KÜLZ.

ALIEN PROPERTY CUSTODIAN

PLASTIFYING OF SYNTHETIC RUBBER

Erich Gartner, Koln-Mulheim, and Albert Koch,
Koln-Dunnwald, Germany; vested in the Alien
Property Custodian

No Drawing. Application filed August 14, 1940

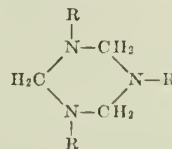
The present invention relates to improvements in the plastifying of synthetic rubber-like materials.

The synthetic rubber-like materials which are obtainable by the emulsion polymerization of butadiene hydrocarbons or of mixtures from butadiene hydrocarbons and copolymerizable vinyl compounds show an inferior plasticity when compared with natural rubber. In consequence thereof, the workability of such products and the incorporation therewith of filling materials, vulcanizing agents etc. is connected with certain difficulties. These disadvantages have been overcome by subjecting the materials described to various desaggregating processes, which effect an increase of plasticity of the unvulcanized products without impairing the mechanical properties of the vulcanizates to any material extent. The plastifying operation which is mostly made use of in practice is by subjecting the polymerizates of the character described to oxidizing conditions in a solid state in the presence of anti-cyclicizing agents. Such processes are described in application Ser. No. 196,903 to Albert Koch and Erich Gartner. This plastifying process can be accelerated by certain auxiliary agents such as phenylhydrazine or the products of the condensation thereof with aldehydes or ketones.

The processes described and in particular the process of application Ser. No. 196,903 represent a distinct advance in the practical use of such polymerizates as a substitute of natural rubber. However, the behavior of such desaggregated and plastified products still leaves something to be desired. It has been observed that the plastified products show a certain recovery from plastification on storing. After a storing over a prolonged period of time, this recovery may be such as to remove for the most part the effect which has been achieved by the application of the plastifying process.

It is the object of the present invention to do away with these disadvantages and to develop a new type of auxiliary agents which allow one to prevent such recovery in an easy and economical manner. Other objects of our invention will be set forth in the following description, it being to be understood that the contents thereof are intended to generally explain our invention without limiting the same in any manner.

The auxiliary agents which are made use of in accordance with our present invention for preventing such undesirable recovery may be defined as 1,3,5-triaryltrimethylenetriamines. These products can be prepared in a manner known per se from an arylamine and formaldehyde in the proportion of 1:1 in the presence of water and in the absence of an acid catalyst. Products of the character described are also defined as anhydroformaldehyde-arylamines and correspond to the following formula



wherein R stands for an aromatic radical such as phenyl, substituted phenyl or naphthyl. These products are incorporated within the synthetic rubber-like materials to be stabilized subsequent to the plastifying process. In general, an amount of about 1 to 3% of the said stabilizing agents is sufficient to exert the desired result. It has been found that the presence of these auxiliary agents brings about a stabilization of the plastified polymeric butadiene hydrocarbons (this term including the mixed polymerizates of the character described) to such an extent that they can be stored for an unlimited period of time. This is true regardless as to whether the synthetic rubber-like materials are stored per se or in form of a non-vulcanized mixture containing filling materials, vulcanizing agents and the like. Such mixtures have proved to be particularly suitable for working the same on the calender and on the tubing machine. In each case, the resulting vulcanizates show excellent mechanical properties.

In the following we are giving some figures illustrating the effect which is achieved by our present invention. The comparative plasticity measurements have been performed in the following manner: A cylinder of the synthetic rubber-like material to be tested of 10 mms in height and in diameter has been loaded at a temperature of 80° C with such a weight as to impart thereto within 30 seconds a deformation to a height of 4 mms. The weights which are necessary for effecting such deformation are given be-

low in grams and are an indication of the plasticity. Moreover, we are giving below the recovery from deformation in % of the deformation (i. e. of 6 mms) which was to be observed within 30 seconds after removing the weight. Such figures are an indication of the elasticity of the unvulcanized product. The plasticizing measurements defined have been described by H. Hagen in "Kautschuk", volume 15, pages 88 to 95, this publication being referred to in "Chemical Abstracts", volume 33, No. 16, column 6647. By way of example, we are giving below the figures which have been obtained with a product of the conjoined emulsion polymerization of butadiene-1,3 and styrene in the proportion of 3:1 which has been subjected to a desaggregation process in the presence of phenyl- β -naphthylamine as anticyclizing agent and thereupon has been stored for several days either per se or in the presence of 3% of a stabilizer of the character described. It is to be understood that these details are by no way limitative and that practically the same result has been obtained by replacing the said rubber-like material by other products of the character described such as those having a lower or higher styrene content and those being free from styrene at all or containing other copolymerizable vinyl compounds than styrene. In the following table, column I shows the behavior of the non-stabilized products and column II that of the stabilized material after a 0, 24, 36, 168, 336, 508 and 672 hours' storing, the first figure in each case representing the deformation in grams as defined above and the second figure the recovery from deformation in % as defined above.

Hours	0	24	36	168	336	508	672
I.....	280/53, 1	310/57, 1	280/55, 1	300/55, 3	280/55, 6	310/59, 2	320/59, 7
II.....	250/52, 7	230/51, 1	240/50	240/50, 2	235/50, 7	230/50, 5	230/50, 3

It follows therefrom that the non-stabilized products show a gradual decrease of plasticity whereas no such effect is to be observed in the case of the stabilized material. This effect appears to be rather independent on the nature of the stabilizing agent provided that it falls within the above definition. The best results have been obtained with those products wherein R stands for phenyl or toluyl, and a somewhat inferior effect with those products wherein the phenyl contains as substituents halogen atoms or other radicals. In the following we are describing some comparative tests which have been performed with various stabilizers of the character described. In this case the solubility of the synthetic rubber in benzene has been taken as an indication of the plasticity as the plasticity as well as the solubility are influenced by the degree of desaggregation. These tests have been carried through by incorporating within an emulsion polymerizate of butadiene and styrene (3:1), which has been desaggregated so as to become soluble in benzene, 3% of various stabilizers, dissolving the said stabilized materials in the 50 fold quantity of benzene each and measuring the time until these solutions show flocculation due to the becoming insoluble of the polymerizate. In the following table column I shows the arylamine which has been employed for the preparation of the anhydroformaldehyde-arylamine serving as stabilizer and column II shows

the time in weeks which has expired until flocculation has occurred:

I	II
p-Toluidine.....	16
p-Chloroaniline.....	12
m-Toluidine.....	6
Mixture of o, m- and p-toluidine.....	6

The stabilizing effect of the auxiliary agents described can be observed also in vulcanizable rubber mixtures so that such mixtures can be stored prior to vulcanization without involving the danger that the workability thereof, for instance on the tubing machine, is impaired. This effect is illustrated by the following table showing the behavior of the following mixture on storing:

Parts	
An emulsion polymerizate of butadiene and styrene (3:1) which has been desaggregated in a manner known per se, for instance by subjecting it to oxidizing conditions at an elevated temperature in the presence of antioxidants.....	90
A low viscous sodium polymerizate of butadiene serving as plasticizer.....	10
Ebonite powder.....	50
Silicic acid.....	15
Mineral oil.....	5
Sulfur.....	32
Condensation product of ethylpropylacrolein and aniline as vulcanization accelerator..	1.5

In the table column I shows the various amounts of anhydroformaldehydeaniline which have been incorporated within the said mixture subsequent to desaggregating, column II shows the plasticity and elasticity of the mixture prior to storing, and column III the same properties of the mixture after a 28 days' storing, the figures having been measured in the manner defined above with reference to the publication by H. Hagen.

I	II	III
0	1500/66	2500/45
0.5	1650/67	2400/74
1	956/57	1450/61
2	525/49	750/50
3	500/42	600/47.5
5	400/46	400/45

In order to avoid any misunderstanding we wish to point out that the stabilizer exerts a certain softening effect on the polymerizate. In consequence thereof, the plasticity of the polymerizate prior to storing is the better the higher a content of the stabilizer is employed.

ERICH GARTNER.
ALBERT KOCH.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF HIGH MOLECULAR POLYAMIDE COMPOUNDS

Paul Schlack, Berlin-Treptow, Germany; vested in the Alien Property Custodian

No Drawing. Application filed August 14, 1940

This invention relates to the manufacture of high molecular polyamide compounds.

When simple bifunctional urethane compounds are condensed in the heat for themselves or together with other substances reactive with urethane compounds, high molecular polyamides are obtained. Such substances were obtained by self-condensation of urethane carboxylic acids with at least 5 atoms between the nitrogen atom and the carbonyl group, by heating of such urethane carboxylic acids with α - ω -diamines, by condensing diurethanes, with $\alpha\omega$ -diamines and finally also by heating of diurethanes for themselves.

There were used until now for the condensation only such urethane compounds, in which the carbamic acid radical is esterified with an aliphatic alcohol. Fundamentally the same reactions show also urethanes with cyclo-aliphatic or aromatic substituted aliphatic alcohols, for instance carbamic acid esters of the benzyl alcohol or of the phenyl ethanol.

It is an object of this invention to produce high molecular polyamide compounds.

A further object is the preparation of filaments, fibers, ribbons from these materials.

Still further objects will become apparent from the detailed specification following hereinafter.

It has been found that the condensation reactions between urethane compounds and other substances condensable together with them proceed by far smoother, when there are used bifunctional starting materials containing the radical of the carbamic acid in esterified form containing at least once the radical of the carbamic acid with an aromatic or enolic hydroxyl compound, and when these products are caused to react at a temperature suitable for the reaction with other bifunctional compounds which show free carboxyl groups or hydroxyl-, sulfhydryl- or amino-groups capable of being acetylated. The reactions take place as a rule already at relatively low temperature and proceed especially in the beginning rather quickly, so that monomeric reaction components not being volatile are not present any more already after a short time. In many cases therefore one can work without excessive pressure, also when relatively volatile substances, for instance 1,4-butylene glycol or diethylene glycol are used. Also when working under pressure advantages are to be found, since displacements of concentrations, caused by distillation are little or not at all to be feared. Furthermore the reaction usually proceeds much more uniformly, as the self-condensation, which happens easily at high temperatures with car-

bamic acid esters of the low aliphatic alcohols, does not occur in this case. It leads also less easily to cross-linking.

The uniformity of the reaction in many cases is of considerable importance, as substances structurally uniform can be more extensively oriented during or after the forming process than irregular mixed condensates or mixtures. Besides that they are usually characterised by a higher melting point. It is therefore easily possible to produce mixed condensates showing a regular arrangement of different components. A very uniform mixed condensate for instance is obtained, when hexamethylene-bis-carbamic acid diphenyl ester (f. p. 133° C.) is condensed with octamethylenediamine or dodecamethylenediamine. This for instance is not as easily accomplished when hexamethylene-bis-carbamic acid dimethylester is heated with octamethylenediamine, or if a mixture of hexamethylenediamine and octamethylenediamine is condensed with a neutral carbamic ester or urea.

Similarly this applies to the condensation with glycols being here of special importance. If for instance hexamethylene-bis-carbamic acid dimethylester is condensed with 1,4-butyleneglycol in equivalent proportions, part of the glycol as a rule remains unchanged on account of the simultaneous self-condensation, whereas when working with the different diarylesters, for instance with the diphenylester or a chlorophenylester, the polyurethane formation proceeds uniformly in the desired way. Simple and substituted phenols are first of all to be mentioned as hydroxyl components for the manufacture of the carbamic acid ester, for instance phenol, m-cresol, the various halogen- and polyhalogenphenols, naphthols, oxydiphenyls. Especially useful are halogen substituted phenols, as they have very little tendency to decolorize.

Instead of the phenols there may be employed with the same success also hydroxyl compounds of other ring systems, in which the hydroxyl group is connected to a double linked carbon atom, for instance oxyppyridine, 4-oxyprazol.

Just as well react the carbamic acid esters of aliphatic or alicyclic enols which may be easily saponified, for instance the carbamic acid esters from aliphatic diisocyanates like hexamethylenediisocyanate and ω -formylacetophenone, from methyl dihydroresorzone or dimethyldihydroresorzone, acetyl acetone, ethyl aceto acetate.

To manufacture carbamic acid esters the corresponding chloroformic acid aryl esters may be caused to act on the amino compounds or when

working under exclusion of water and in the heat on their salts, especially when the latter contain hydrogenhalide. In the latter case it is of advantage to employ an indifferent solvent, for instance benzene, toluene, chlorobenzene. Furthermore they are obtained by a reaction of the amino compounds with the corresponding carbonic esters, whereby it is useful to discharge gradually the amine into a solution of the carbonic ester. It was found hereby that for uniform course of the reaction it is of great importance, if a solvent is chosen, in which the carbamic acid ester to be expected is as little soluble as possible. Especially suitable are hydrocarbons like benzene or chlorobenzene. The carbonic ester may preferably be used in excess, if for instance the reaction product on account of the solubility may be easily separated from the excess of the ester.

Needless to say the carbamic acid esters are also obtainable by a reaction of phenols with isocyanates or the corresponding carbamic acid chlorides. As far as amine compounds with a secondary amine nitrogen are concerned it is best to work with carbamic acid chlorides.

Derivatives of secondary amino compounds, for instance carbamic acid esters from symmetric dimethyltetramethylene-diamine are preferably suited for the reaction with amino compounds, for instance hexamethylenediamine.

For the condensation in principle also such carbamic acid esters may be used, the carbon chains of which are interrupted by so called hetero atoms or groups like O, S, N, SO₂. To insert also sulfamide groups into the carbon chain of the carbamic acid ester is possible according to German Patent application I. 64 124 / 12 o, filed March 20, 1939. In the same way also the bifunctional compounds condensable with the carbamic acid esters, for instance the diamines or glycols may contain such groupings or atoms interrupting the chain.

In order to produce condensation products, nearly equimolecular quantities of the components are heated in the presence or absence of a solvent. As a rule it is useful to start the condensation at a relatively low temperature and to apply higher temperatures only then, if the monomeric starting materials have practically disappeared. The oxy compound which is split off, for instance a phenol, may be distilled off at the end, if one does not prefer to work up the finished polyamide with a precipitant, if necessary after dilution. A working method practical in many cases is to employ the carbamic acid ester of an oxy compound being solid at room-temperature and to remove the split off oxy compound with a solvent, for instance acetone, after disintegration by grinding from the finished solidified polyamide. The reaction product remains then in the form of a coarse powder, which can be moulded.

The products separated by precipitation may be again condensed by remelting and reheating at correspondingly high temperature, preferably in vacuo. Hereby also a small amount of bifunctional acid forming compounds are preferably added, for instance dicarboxylic acids like sebacic acid, or diamines like hexamethylenediamine.

The condensations may be increased and facilitated especially in the production of polyurethanes by adding catalysts, for instance small amounts alkali alcoholate, alkali phenolate, tertiary amines or acid reacting compounds like

hydrogen halide, aryl sulfonic acids, hydrohalic acids of amines and amino acids. Especially when condensing with amino compounds the degree of the desired condensation may be extensively influenced by adding acid compounds, for instance amino hydrochlorides, amino-acid-hydrochlorides, -phosphates, -toluenesulfonates.

The high molecular condensation products according to the present invention may be worked up into filaments, ribbons, foils, directly from the melt or from the solutions, for instance in phenols, acetic acid, formic acid, and the like. The spun filaments, especially those obtained directly from the melt, show high elasticity and obtain excellent tenacity by the drawing process. Structures may be also obtained from the polyamides by casting, dye-casting, injection moulding or pressing.

Example I

1 mol hexamethylene diisocyanate is dissolved in 2.5 parts phenol, whereby the diurethane is formed. There is then added 1 mol 1,4-butane-diol and $\frac{1}{200}$ mol lithium phenolate. The mixture is then heated up to 160° C for 3 hours. The phenol is distilled off in vacuo (1-2 mm). The last parts of the phenol are removed in vacuo by conducting over large surfaces the liquid now heated at 220° C in the presence of nitrogen, the melt for instance is thereby caused to flow through an evacuated funnel in the form of a film. The mass melting at 175° C may be directly spun. The process may be performed continuously.

Example II

1 mol hexamethylenediamine in 5 times the quantity of benzene is added at 80° C, while stirring, to a solution of 1 mol diphenylcarbonate also in 5 times its quantity of benzene. When standing, the hexamethylene-bis-carbamic acid diphenyl ester is separated in colorless crystals (f. p. 138° C). It can be recrystallized from hot benzene.

1 mol of this carbamic acid ester is mixed with $\frac{1}{200}$ mol lithium phenolate and 1 mol diethylene glycol, then heated at 100° C for 2 hours and finally at 140° C for 5 hours. The reaction product is dissolved in glycol monomethyl ether and precipitated with acetone.

Example III

1 mol tetramethylene diamine, then 1 mol tetramethylene glycol is added to a 20% solution of polymeric ϵ -caprolactam (2 mols) in phenol. The mixture is then caused to flow continuously through a tube heated at 150° C, then through another tube heated at 180° C which, if necessary, is rotatively constructed. After the mass has left the two tubes within 4 hours, it flows into an inclined vacuum vessel, evacuated at about 2 mm. As described in Example I, the mass flows here over a large heating surface, whereby the last portions of the phenol and monomeric lactam are evaporated. The homogeneously melting mass is finally fed to the spinnerets by pumps.

Example IV

2 mols chloroformic acid phenyl ester are added to a solution of 1 mol hexamethylene diamine in chlorobenzene. The mass is heated until the development of hydrogenchloride ceases. When working it up the hexamethylenedicarbamic acid diphenyl ester remains in colorless crystals (f. p. 138° C). 1 mol of the diurethane is melted with 1 mol sebacic acid and heated first at

180° for 3 hours, then at 240° C still another 3 hours in vacuo (2 mm), whereby the phenol is distilled off. The polyamide thus obtained is excellently spinnable from the melt.

Example V

1 mol hexamethylene-bis-carbamic acid diphenylester is melted together with 1 mol octamethyl diamine. The melt is heated gradually at 180° C and kept at this temperature for 3 hours. The phenol is distilled off in vacuo under exclusion of atmospheric oxygen, whereby the temperature is gradually raised up to 240° C. The reaction product is a hard, nearly white resin which is easily formed by mechanical means. It is not identical with the product obtained when 1 mol hexamethylene diamine and 1 mol octamethylene diamine are condensed together in the heat with 2 mols butylcarbonate.

Example VI

Half a mol ϵ -amino caproic acid methyl ester in benzene is added, while cooling, to a solution of 1 mol chloroformic acid phenyl ester in benzene. After the benzene is distilled off the ϵ -phenylcarbaminyl caproic acid methyl ester is separated from the amino caproic acid methyl ester hydrochloride by adding water. The dried urethane ester (1 mol) is then mixed with 1 mol hexamethylenediamine and heated at 100° C for 2 hours, then at 240° C for further 4 hours and finally heated in vacuo. The polyamide thus obtained can be spun from the melt.

Example VII

Hexamethylenedimercaptane is melted with the calculated amount hexamethylene-bis-carbamic acid diphenyl ester and the melt heated at 150° C for 3 hours. Then the phenol thus formed is distilled off in vacuo (2 mm) at a bath temperature increasing from 150–200° C. in a nitrogen atmosphere free from oxygen within 3 hours. The remaining melt may be formed into elastic filaments which may be oriented by drawing.

Instead of the mercaptane also one of its salts, for instance the lithium compounds may be employed. There is formed the respective phenolate as by-product. This is washed out with alcohol from the melt which solidifies, when cooled down. Also amine salts of mercaptanes may be employed. Volatile amines are then distilled off together with phenols.

Example VIII

2 mols chloroformic acid phenyl ester are dissolved in o-dichlorobenzene and there is added gradually 1 mol hexamethylene diamine dissolved in o-dichlorobenzene. The hexamethylene diamine hydrochloride and more or less also hexamethylene dicarbamic acid phenyl ester is hereby precipitated. The mass is heated, while stirring, until all is again dissolved. Then there is added 1 mol decamethylene glycol. The mass is then heated at 150° C for 5 hours. the temperature then increased for 1 hour until boiling and the solvent and the phenol thus formed is distilled off in vacuo, whereby the temperature is finally raised up to 220° C. The liquid residue is then extruded by a nozzle as skein into cold water.

Example IX

Symmetrical dimethyl-1,4-tetramethylene diamine is transformed with phosgene in the usual way in tetramethylene-bis-carbamic acid chloride and the latter converted by heating with phenol dissolved in benzene into the tetramethylene-bis-carbamic acid diphenyl ester. After the hydrogen chloride development is finished, the equivalent amount $\beta\beta'$ -diamino-diethylether is added. The benzene is distilled off, the residue heated to 180° C within several hours. The phenol thus separated is finally distilled off in vacuo. The product thus obtained may be drawn into filaments from the melt.

PAUL SCHLACK.

ALIEN PROPERTY CUSTODIAN

COSMETIC FOR HAIR AND SKIN

Siegfried Wiechowski, Vienna, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed August 14, 1940

This invention relates to a process for the production of a lasting biological cosmetic for hair and skin, which possesses a high efficiency for preserving the sound skin and for healing diseased skin, and especially for promoting the growth of hair and for preserving hair, owing to its content in valuable natural substances. The fundamental idea of the process according to the invention consists in that active substances present in sound hair are to be used for the preservation and culture of the skin and especially of the hair.

To attain this, the keratosenic product from hydrolysis, obtained by hydrolysis from hair at 50-70° C, is neutralized with one or several fatty acids and/or fats without previous isolation or precipitation, directly after its formation.

The dissolving of hair by hydrolysis with the acid of lyes is known. It has already been known to dissolve hair in strong solutions of alkali, that is in a lye of approximately 50%, to precipitate the dissolved substances, to separate and to dry the same and to mix them with oils or pomades to form a hair cosmetic. Such cosmetics possess, however, no effect for stimulating the growth of hair for the reason that, by the action of strong alkali solutions, the constitution of the extremely sensitive keratosenic products is influenced so that these products are decomposed very much and lose their properties to promote the growth of hair.

In order to avoid this and to attain, that the efficient substances existing in the hair are preserved as far as possible in the original form, that is in the form nearest to nature, the hair is dissolved, according to the invention, by very careful hydrolysis with accordingly diluted lyes at a moderate temperature of about 50-70° C, whereby the formation of the sensitive active substances is not impaired. As, however, such solutions are not lasting, owing to the fact that they decompose easily and thereby become ineffective for the process according to the invention, the keratosenic products are converted, directly after their formation without isolation or precipitation, into a solid neutral substance by

means of fatty acid whereby the active substances are fixed. As fatty acids can be employed liquid acids, but preferably solid acids, singly or in a greater number. It has further been found that, instead of fatty acids, fats may be employed which are split by the alkaline solution, the formed fatty acids entering into reaction with the hydrolysates. It is, however, possible to bring into reaction with the alkaline solution one or several fatty acids or fats at the same time.

As numerous clinical experiments and the practice have shown, the product obtained according to the invention exerts a healing effect upon the skin, owing to its content in active substances specific for the skin and for the hair, as in this manner these substances are supplied to the epidermis in natural form, that is as much as possible in a form not altered by the present process, which are necessary for the growth of the hair and for maintaining it in sound state.

According to the invention it is especially advantageous if, for the culture of the hair on the head, the hair-keratosen-preparation is used simultaneously with washing of the skin. A fatty skin becomes thus free from fat and strongly receptive for the cosmetic prepared according to the invention. With this object in view the solid keratosen product of the hair is mixed with a neutral soap, whereby two advantages are obtained at the same time. Firstly the skin becomes free from fat by the washing with soap and secondly the soap foam, owing to the emulsification of the keratosenic product, facilitates penetration into the skin of the head and the absorption by the hair papillas.

Example

1000 gr of washed hair are brought to solution in 5000 gr. soda lye (12 Be) at about 50-70° C. 2300 gr of molten stearin acid (or stearin) are added to the solution which is still in hot state and which must not be heated to above 70° C, the mixture is stirred and mixed, while it is still in liquid state, with 50 kgs of neutral kernel.

SIEGFRIED WIECHOWSKI.

ALIEN PROPERTY CUSTODIAN

PREPARATION OF CROTONALDEHYDE

Martin Mueller-Cunradi, Hellmut Giehne, and
Heinz Krekeler, Ludwigshafen-on-Rhine, Ger-
many; vested in the Alien Property Custodian

No Drawing. Application filed August 20, 1940

The present invention relates to improvements in the preparation of crotonaldehyde. In particular it relates to the crotonisation of acetaldol by the action of heat on crude acetaldol solutions as obtained in the aldolisation of acetaldehyde.

It is an object of this invention to provide a practical, economical and commercially applicable method for the preparation of crotonaldehyde in a continuous process. It has been known for some time that crotonaldehyde may be prepared by introducing aldol into a boiling dilute acid solution and removing the decomposition products substantially as fast as formed. In order to promote the expulsion of the decomposition products it has also been proposed to carry out the crotonisation under sub-atmospheric pressure while using lower temperatures. The decomposition products of the crotonisation consist substantially of crotonaldehyde and water, provided that the aldol used was free from other constituents. In practice, the decomposition products are admixed with acetaldehyde which is always present in the crude aldol usually employed in the preparation of crotonaldehyde. Hence, during the step of condensing crotonaldehyde and water from the vapors distilling off from the crotonising vessel, care has to be taken that the acetaldehyde is also condensed. When operating under normal pressure, the condensation of acetaldehyde requires a cooling medium of low temperature. In a vacuum process, it becomes necessary to use brine in order to avoid substantial losses of acetaldehyde.

We have now found that the crotonisation of crude aldol may be carried out with excellent yields in a very simple manner, by exposing the liquid aldol to the action of heat in a crotonising vessel under superatmospheric pressure. Generally speaking, the pressure used may only be from 0.5 to 2 atmospheres in excess of atmospheric pressure, though higher pressures may likewise be employed.

In preparing crotonaldehyde according to our invention, crude aldol as obtained by treating acetaldehyde with aqueous alkaline solutions may be admixed continuously with an agent promoting the splitting off of water and be pressed into a fractionating device kept under superatmospheric pressure. The crotonisation products obtained (including acetaldehyde) are separated by fractional distillation under superatmospheric pressure, the crotonisation thus taking place during the fractionation.

Crude aldol may also be introduced continuously into a still connected with a fractionating

column kept under superatmospheric pressure, the still being charged with an aqueous solution of a crotonising agent. This solution is heated to a temperature enabling the crotonisation products to be distilled off. The speed of distillation is so chosen that the concentration of the crotonising solution remains substantially constant during the process. The vapors emerging from the solution consisting substantially in an azeotropic mixture of crotonaldehyde and water and in acetaldehyde are separated in the single constituents by means of the fractionating column and obtained in the liquid form. The acetaldehyde obtained may again be used for preparing aldol. The crotonising agent may be added to the crude aldol before it is introduced into the reaction vessel.

According to our invention it is possible to condense the acetaldehyde distilling off together with crotonaldehyde and water simply by means of water of ordinary temperature as cooling medium, whereas when working under normal or subatmospheric pressure, special cooling agents are necessary. It is surprising that the speed of crotonisation is not affected by working under superatmospheric pressure and that the crotonaldehyde formed does not undergo any side-reactions.

The following example will further serve to illustrate the nature of our invention, but the invention is not restricted to this example. The parts are by weight.

Example

A solution of 5 parts of primary sodium phosphate in 100 parts of water is kept boiling in a distillation still provided with a fractionating apparatus under a pressure of 0.8 in excess of atmospheric pressure. 160 parts of a mixture of aldol and acetaldehyde, containing 76 parts of aldol, per hour are introduced into the still. A mixture of water, crotonaldehyde and acetaldehyde distills off at the same rate. There are obtained 60 parts of crotonaldehyde per hour, and 84 parts of acetaldehyde per hour, the latter being condensed at 35° C by means of water of 25° C as the cooling agent. Crotonaldehyde and water leave the fractionating device in the liquid form. The acetaldehyde is led back for aldolisation.

The primary sodium phosphate in the above process may be replaced by other electrolyte solutions exerting a from acid to neutral reaction. There may be used, for example, diluted mineral acids, organic acids or salt solutions having a

from acid to neutral reaction. Preferably, the crotonisation should be carried out in an aqueous solution having a pH-value within the range from 2 to 7. In order that this range is maintained during crotonisation, it is preferable to use electrolyte solutions which have a buffering action within that range. The preparation of such buffering solutions is generally known; we prefer to use, for example, primary and secondary alkali

metal phosphates or mixtures thereof or these phosphates admixed with small amounts of free phosphoric acid, or potassium bifluoride or, in case the aldol used has already a weakly acid reaction, sodium acetate.

MARTIN MUELLER-CUNRADI.
HELLMUT GIEHNE.
HEINZ KREKELER.

ALIEN PROPERTY CUSTODIAN

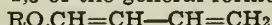
PROCESS FOR THE POLYMERIZATION OF ALKOXY-BUTADIENES

Paul Halbig, Freiburg, Switzerland, Friedrich
Matthias and Alfred Treibs, Munich, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed August 23, 1940

The addition of alcohols to vinylacetylene is known. Thereby products were obtained being interpreted partly as butine derivatives, partly as allene derivatives and partly as alkoxy-2-butadienes. Useful polymers could not yet be produced out of these compounds. Experiments of polymerization were nearly always negative, compare e. g. Rothenberg Zentralblatt 1936, II, p. 1895.

We have now found, applying kalium-alcoholate as catalyst, a new class of alcohol addition products of vinylacetylene not known until now which surprisingly polymerizes easily. They have, as stated by us, the constitution of alkoxy-1-butadiene-1,3 of the general formula



whereby OR may be any kind of alcohol. By discovering effective catalysts used successfully for alkoxy-1-butadienes, we were able to realize the polymerization of alkoxy-2-butadienes. Mixtures of 1- and 2-alkoxy-butadienes are also polymerizable.

Specially suitable polymerization catalysts are kapillar-active substances like above all clay, kaolin and kapillarractive hydrosilicates known f. i. under the name of Tonsil, Frankonit, Floridin and the like. The polymerization is not accelerated by all of these substances, active carbon and silicagel scarcely act. As polymerization catalysts quite different substances however also may be used, especially some metal chlorides like $FeCl_3$, $AlCl_3$, $ZnCl_2$ and boron fluoride. Acids like hydrochloric acid, sulfuric acid, nitric acid, phosphorous pentoxide also cause polymerization. Elementary oxygen and the known peroxyde accelerators catalyze the polymerization. Further on the polymers themselves are polymerization catalysts. These catalysts can be employed as suspensions or solutions.

The properties of the polymerization products may be largely varied by means of the numerous methods applied in the art of polymerization of to-day, according to the intended use. Such means are f. i. the polymerization at defined temperatures with or without any solvents, the polymerization of the monomeric compound in an emulsified state, the polymerization of the monomeric compound with other polymerizable substances or with substances not polymerizing per se, the polymerization in the presence of polymers of other substances and the variation of the amount and composition of the polymerization catalysts, and so on.

Above all it is important that there is the possibility of polymerizing the alkoxy-1-butadiene

with substances polymerizing per se as f. i. acrylic nitril, 1- and 2-acetoxy-butadiene, linseed oil or also with such ones polymerizing only in special cases together with other substances, as f. i. maleic anhydride. The reaction of alkoxy-2-butadiene with maleic acid anhydride has already been tried, obviously with the intention to perform a "diene-synthesis", but only a dark resin was obtained thereby under violent reaction. By the method of working applied by us, however, light elastic interpolymers are obtained with 1- and 2-alkoxy butadiene which according to the presence of functional groups may further be converted into derivatives of carbon acids. Partly the polymers are also oils with drying properties. In many cases the polymers are rubberlike, that is they are vulcanizable; they can chiefly be applied in the lacquer-industry and for artificial resins. The interpolymers comprise the whole scope of artificial resins which are oillike, rubberlike and resinlike.

Example 1

0,1 g of fine powdered kaolin are added to 10 g of ethoxy-butadiene at room temperature. The polymerization begins slowly; the temperature rises and solid polymerization products are precipitated. The temperature rises to the boiling point and the heat is removed by cooling. After few minutes the polymerization is finished. The polymer is a colorless till slightly yellow, rubberlike and slightly sticky mass which can be vulcanized by sulfur or other suitable means.

The ability of polymerizing depends on the purity of the ethoxy-butadiene that is the inclination of the product to polymerize increases with the increasing purity of the product. Butadiene ethers too react in the same way. The activity of the catalyst may be increased by previous heating; unglazed, burnt clay is a suitable catalyst too. The polymerization with pure substances and high active kaolin, used as catalyst, proceeds so violently that larger amounts overheat themselves until decomposition, if the reaction heat is not removed. The thus obtained polymers are for the most part very high molecular and unsoluble but swellable in solvents. Low molecular constituents can be extracted by ether. The course of the polymerization may be moderated by the addition of solvents.

In the same way alkyl-homologs of the ethoxy-1-butadiene may be polymerized f. i. methoxy-, propoxy-, butoxy-butadiene and the like. The polymerization is scarcely influenced by anti-oxidation catalysts as f. i. hydroquinone. The

methoxy-1-butadiene, boiling point: 87.5° C/703 mm D₄²⁰:0.8296, polymerizes somewhat more slowly than the ethyl derivative which shows the greatest ability of polymerizing. The polymerization velocity of the ethers with higher alkyl groups decreases when the alkyl groups increase.

Example 2

In a vessel, equipped with a stirrer, 50 parts by weight of benzene together with 0.6 parts by weight of kaolin are heated up to the boiling point and a mixture of 10 parts by weight of ethoxy-1-butadiene and 30 parts by weight of benzene are added dropwise. After 15 minutes a white gel-like mass begins to precipitate. The reaction is finished after a further hour. The solvent may be removed by water steam or by distillation. The remaining polymer is a nearly colorless, elastic mass. Instead of benzene other solvents such as ethyle acetate, carbon tetrachloride, methylene chloride and others may be used.

Example 3

Hexoxy-1-butadiene is solved in the same amount of benzene and heated with 1% of Floridin till to the boiling point. The working up takes place as shown in Example 2. A light elastic mass is obtained.

Example 4

Ethoxy-1-butadiene is heated with 0.5% of zinc chloride to 60° C under stirring. The resulting polymer is a thick, tough mass. Salts like aluminium chloride, iron chloride and other react similarly. The polymers are partly soluble, for the most part, however, they are insoluble in the usual solvents like benzene, acetone, alcohol, ethylacetate, and the like.

Example 5

1% of kaolin is added to ethoxy-2-butadiene and heated up in a pressure vessel to 100° C for 8 hours. A rubberlike polymer is obtained.

Example 6

2% of kaolin are added to a mixture of 9 parts by weight of ethoxy-1-butadiene and 1 part by weight of ethoxy-2-butadiene.

The polymerization is started by heating whereby the temperatures of the reaction must not be allowed to rise above 80°. When the temperature begins to decrease the polymerization by heating. The polymer is a light elastic mass.

Example 7

A molar amount of maleic anhydride is added to a solution of butoxy-1-butadiene in the double volumen of benzene; the mixture is heated whereby the sulfur-yellow solution becomes colorless. The very viscous solution yields after the evaporation of the benzene a rubberlike elastic mass. The polymer is vulcanizable.

Without diluents the alkoxy-1-butadiene react so violently with maleic anhydride that decomposition takes place. The reaction may easily be regulated by the addition of inert diluents. The interpolymers with larger alcohol groups show better solubility than those with smaller ones. The solubility also depends on the course of reaction and the after-treatment. If the solution is evaporated by a higher temperature the products cannot be solved in such an easy manner. Products being soluble in a specially easy manner are obtained if the reaction is executed rapidly and

with few solvents. The polymers swell extraordinarily well in lyes; the low molecular products yield high viscous solutions. The anhydride groups of the polymers can be converted with compounds reacting generally with anhydride as f.i. alcohols, amines and the like, whereby derivatives of the interpolymers are obtained. By this way the properties of the polymers may be varied.

Example 8

Molar amounts of ethoxy-1-butadiene and maleic anhydride are polymerized in the same amount of benzene as in Example 7. Hereafter an amount of ethylene glycol, corresponding with 1 mol, is added and the mixture is boiled under reflux as long as a homogeneous solution is obtained. By evaporating the solvent the ester of the interpolpolymer is obtained.

Example 9

In a vessel equipped with a stirrer are 5 parts by weight of boiling benzene and 0.06 parts by weight of kaolin. A mixture of 10 parts by weight of ethoxy-1-butadiene and a solution of 1 part by weight of maleic anhydride in 11 parts by weight of benzene is added dropwise. The polymerization is finished after 1 hour. A product of rubberlike properties is obtained after evaporating the solvent.

Example 10

Ethoxy-2-butadiene is brought to reaction with maleic anhydride in a boiling etheric solution. At the beginning of the reaction the solution is intensively yellow but when the polymerization proceeds the solution becomes more and more lighter. A high elastic product is obtained after evaporating the solvent at 100°. Another course of polymerization runs as follows: ethoxy-1-butadiene is solved in the same volume of benzene and the molar amount of maleic anhydride is added. After standing for 24 hours the yellow color disappears and a thick solution of the nearly colorless interpolpolymer is obtained.

Example 11

A slow current of oxygen is conducted at room temperature through butoxy-1-butadiene. After 12 hours a polymer in form of a thick colorless oil is obtained out of which still some monomeres may be removed by water steam. The oil has the property of drying and yields with the usual siccatives hardening films. Similar products are also obtained by the other alkoxy-1-derivatives of butadiene. The alkoxy-2-derivatives react correspondingly. The ethyl-glycol-ethers of the oxy-1-butadiene (boiling point 66-67°/9 mm D₂₀⁴: 0.8970, of intensive odor of cress) and the oxy-2-butadiene (boiling point 54-55°/9 mm D₂₀⁴: 0.8983, of aromatic odor but quite different from the odor of the 1-derivative) polymerize in a specially easy manner under the influence of air oxygen.

Example 12

Ethoxy-1-butadiene is boiled with 0.5% of benzoyl peroxyde. After 30 hour a viscous fluid is obtained still containing somewhat unpolymerized ether.

Example 13

Pure ethoxy-1-butadiene is heated up to 120° in a pressure vessel. After 5 hours a thick colorless oil is obtained which is formed within a shorter time if the temperatures are higher.

Example 14

Oxygen is conducted at room temperature through cyclohexoxy-1-butadiene and the mixture is allowed to stand. After 3 days a thick colorless oil is obtained.

Example 15

1- α -Ethyl-hexoxy-butadiene is shortly treated with oxygen as shown in Example 14 and hereafter heated up to 100°. After some hours a thick colorless oil is obtained. The same result is obtained with the n-hexoxy-derivative.

Example 16

100 parts by weight of ethoxy-1-butadiene are 15

stirred with 200 parts by weight of petrolether and 1 part by weight of kaolin at 0°. After 3 days the essential amount is polymerized. The white polymer, unsoluble in petrolether, is separated from 5 petrolether and extracted with new one.

Example 17

Ethoxy-1-butadiene is heated up to 130° with half the amount of acrylic-nitril in a closed vessel 10 for 6 hours. A thick oil of a slightly yellow color is obtained.

PAUL HALBIG.

FRIEDRICH MATTHIAS.

ALFRED TREIBS.

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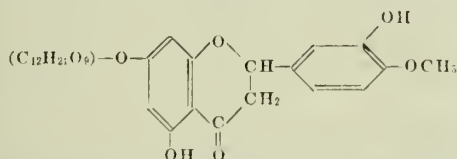
PROCESS FOR PREPARING A DERIVATIVE OF HESPERIDIN

Masaki Ohta, Osaka, Japan; vested in the
Alien Property Custodian

No Drawing. Application filed August 26, 1940

This invention relates to improvements in a process for preparing a derivative of hesperidin, which is a new chemical substance, soluble in water and useful for therapeutical purpose.

Hesperidin (5-7-3' - trioxy - 4' - methoxyflavone glucoside) which has the constitutional formula

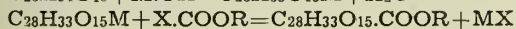
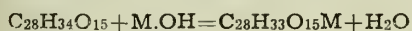


has pharmacological effects, but it is hardly soluble in water, alcohol and other ordinary solvents at room temperature so that it is very inconvenient for handling.

When an aqueous solution of an alkali, e. g. potassium hydroxide or sodium hydroxide, is added to hesperidin, the latter is dissolved and produces its alkali salt, which when treated with an alkyl halogen carbonate such as ethyl chlorocarbonate in a solvent, alcohol, benzol, etc., a reaction takes place separating halogen alkali and a carbalkoxyl radical is introduced.

This product is a new chemical substance which is easily soluble in water, hot alcohol and hot ethyl acetate, and its aqueous solution shows a reddish brown colour by ferric chloride. If metallic magnesium is added to its alcoholic hydrochloric acid solution a blight red colour appears.

The chemical reactions above mentioned are shown by the following formulae.



In these formulae, the notation M represents

an alkali metal, X represents halogen atom and R alkyl radical.

Example 1

10 parts of hesperidin are dissolved in about 150 parts of 2% aqueous solution of potassium hydroxide, to which 4 parts of ethyl chlorocarbonate are added and is kept alone for a few hours. A very small quantity of sediment produced is removed by filtration and the filtrate is evaporated under vacuum when a viscous residue is obtained.

This residue is extracted with hot alcohol so as to remove insoluble potassium chloride, and a jelly-like sediment is obtained when the alcoholic solution is cooled. This sediment is collected by filtration and is re-crystallized from alcohol. When the product is dried in vacuum at 100° C, 8 parts of slightly yellowish powder are obtained, which melts at 135° C under decomposition. It is ascertained by analysis that this is a new chemical substance having the chemical formula $\text{C}_{31}\text{H}_{38}\text{O}_{18}$.

This new substance is easily dissolved in a dilute caustic alkali solution and produces hesperidin, the starting material. If it is boiled with a mineral acid, sugars and aglycon are produced.

Example 2

10 parts of hesperidin are stirred for an hour with a solution of 8 parts sodium in 500 cc. alcohol, then 4 parts of ethyl chlorocarbonate are added and the mixture is refluxed for two hours. Sodium chloride produced therein is filtered off while hot, and the alcoholic solution is evaporated until it gets to a small amount, from which jelly-like precipitates are obtained. Recrystallizing from alcohol, the same product as of the Example 1 is obtained. The yield is 7 parts.

MASAKI OHTA.

ALIEN PROPERTY CUSTODIAN

METHOD FOR THE PRODUCTION OF POLY- CONDENSATION PRODUCTS, AND THE RE- SULTANT PRODUCTS PRODUCED THERE- FROM

Otto Moldenhauer and Helmuth Bock, Hirschberg
Riesengebirge, Germany; vested in the Alien
Property Custodian

No Drawing. Application filed September 4, 1940

This invention relates to a method for the pro-
duction of polycondensation products, and the re-
sultant products produced therefrom, and more
particularly to the production of said products
as are adapted to be worked into fibers and films.

The object of this invention is the provision of
a new method for the production of polyconden-
sation products, adapted to be worked into fibers
and films.

The basis of the new method and products
forming the present invention, lies in the use of
semi-carbazides such, for example, as thiosemi-
carbazides, either by themselves alone or in com-
bination with dicarboxylic acids or their deriva-
tives. These compositions have been found to
produce particularly good fiber-forming polymer-
ization products.

In accordance with one form of the invention,
a mass particularly adapted to the drawing of
fibers may be produced by the self-condensation
of pure semi-carbazides by heating the same in
a high vacuum to a higher temperature.

Instead of using a semi-carbazide alone, the
latter, as in the form of thiosemi-carbazide can
be melted together with dicarboxylic acid or one
of its derivatives. As an example of this process,
one may obtain a fused mass by the double de-
composition of adipinic acid anhydride with thio-
semi-carbazide at a temperature of approxi-
mately 200° C, which will permit itself to be read-
ily spun into fibers.

More specific examples of the method and
products in accordance with the present inven-
tion are as follows:

Example 1

92 parts of sebacic acid anhydride are ground

together with 45 parts of thiosemi-carbazide and
melted together at 200° C. After a short heating
period of approximately 20 minutes a decomposi-
tion takes place. There is then produced a
brown-colored product having a softening point
of 70° C, which can very easily be spun.

Example 2

258 parts of adipinic acid butylester and 90
parts of thiosemi-carbazide are transposed in the
presence of sodium alcoholate for four hours in
an autoclave at 200° C. The butanol which is
produced by this process is preferably distilled off
in a vacuum, and there will result a plastic,
easily spinnable mass.

Example 3

128 grams of adipinic acid anhydride are
ground intimately with 75 grams of semi-carba-
zide and heated quickly in a vacuum of approxi-
mately 1 mm. mercury. The mixture is con-
densed approximately three hours until an en-
tirely clear melt is produced.

The condensation products formed as set forth
above have good plastic characteristics. They
also permit themselves to be readily worked into
fibers or films. The fibers so produced, however,
are quite soluble in water, but this may be cor-
rected by a special supplemental treatment as is
well known in the art, if the fibers are to be used
for textile purposes.

OTTO MOLDENHAUER.
HELMUTH BOCK.

ALIEN PROPERTY CUSTODIAN

SOLUTIONS OF POLYAMIDES

Kurt Thinius, Ellenburg, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed September 4, 1940

This invention relates to new compositions of matter and more particularly to a new and valuable process for the production of solutions and pastes comprising synthetic linear polyamides.

These polyamides, the utility of which is enhanced by the practice of this invention, are of two types, namely those derived from monoamino monocarboxylic acids and their amide-forming derivatives, and those derived from the reaction of suitable diamines with suitable dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids. It will be noted that the polyamides are derived from the functional amide-forming derivatives. Mixed polycondensation products are also obtained by heat-condensation of bifunctional compounds. There are condensed for instance ω -aminocarboxylic acids with at least five chain-forming atoms between amino group and carboxyl group or their amide-forming derivatives, such as esters, chlorides, lactams, furthermore diamines with four and more carbon atoms between the two amino groups and finally dicarboxylic acids with at least three, preferably more carbon atoms between the two carboxyl groups or their amide-forming derivatives. The condensation products thus obtained are at ordinary temperature insoluble in aliphatic and aromatic hydrocarbons, chloro-hydrocarbons, esters, ketones, in the simple monohydric and polyhydric alcohols, their ethers and also in cyclic ethers.

According to German patent application I 64 433 IVd/12o, filed April 24, 1939, it has been proposed to bring into solution by heating with an aliphatic alcohol the mixed-condensates obtained from dicarboxylic acids and diamines on the one hand and ω -aminocarboxylic acids or their functional derivatives on the other hand. However, when cooling at room-temperature these solutions are not stable and can be worked up with great difficulties only. In order to work up the polyamides by means of a solution it is therefore necessary to use their feebly basic properties and to employ acids as suitable solvents. Though it is possible by this method to obtain a solution already at normal temperature, it is rather inconvenient to work with strongly acid agents. It also may be left undecided whether or not far reaching changes of the polyamide molecules are brought about by the effect of the acid.

This invention has as an object, therefore, the preparation of solutions and pastes from mixed-polycondensation products of dibasic acids, diamines and ω -aminocarboxylic acids.

Further objects will appear hereinafter.

It has been found that polyamides obtained by mixed-condensation of dicarboxylic acids with diamines of four and more carbon atoms between the amino groups and with ω -aminocarboxylic

acids of five and more carbon atoms between the amino- and the carboxyl group or their amide-forming derivatives, such as lactams, esters, acid chlorides, can be dissolved in ethylene chlorohydrine (β -chloro ethyl alcohol) at normal temperature within a very short time. In this way clear solutions free from structures are formed. Preferably there are employed mixed-condensates being formed from adipic acid, hexamethylene diamine on the one side and ϵ -caprolactam on the other side. Most suitable are such mixed-condensates which contain at least 40% and not far above 60% of the total weight in the form of ϵ -caprolactam. Since the chlorohydrine represents an acid-free liquid, all disadvantages connected with the handling of acid liquids are overcome, when working up the solutions prepared thereof. The 25%-solutions of the polyamide in ethylene chlorohydrine leave, for instance, behind after evaporation of the solvent a clear and solid film. Whereas the solutions of the polyamide in inorganic or organic acids are already precipitated by small quantities of water, alcohol or similar liquids, even concentrated solutions of the aforementioned polyamide in ethylene chlorohydrine may be mixed without any coagulation with liquids containing hydroxyl, water, alcohols, especially ethyl alcohol. On the contrary these solutions are capable of peptizing further quantities of polyamide. Also the water soluble ethers of the ethylene glycol, for instance the methyl glycol and esters containing hydroxyl may be added in very large quantities to these solutions. Also in these cases the capability of peptizing still further quantities of polyamide has remained. This was highly surprising as for instance methyl glycol does practically not dissolve the polyamide even at 80° C. and also the lactic acid ester for instance does not dissolve it at elevated temperature. The solutions of the polyamide in ethylene chlorohydrine show towards hydrocarbons, esters, ketones, ethers, cyclic ethers and acetals reduced dilution capacity. When using simultaneously liquids containing hydroxyl and representatives of the aforementioned group of substances, it is quite easy to manufacture lacquers from the polyamide, the evaporation curves of which follow the usual rules of spraying- and painting technic. The solutions of the polyamide in ethylene chlorohydrine may be mixed up with plasticizers, pigments and dyestuffs in a known manner. They may be employed then as coating material for structures of any kind, such as paper, textiles, wood, metal, also for the manufacture of artificial leather, floor coatings, motorcar tops and the like. Needless to say it is also possible to work up the solutions into films, foils, filaments, sound records, bristles and similar structures.

KURT THINIUS.

ALIEN PROPERTY CUSTODIAN

SEPARATION PROCESS

Friedrich Asinger, Leuna, Roderich Graf, Frankfurt-on-Main, Paul Herold, Leuna, Carl Platz, Frankfurt - on - Main, and Walter Schmidt, Leuna, Germany; vested in the Alien Property Custodian

No Drawing. Application filed September 7, 1940

According to a known method organic compounds, in particular hydrocarbons, can be converted into compounds containing sulfur, oxygen and halogen by acting thereon with sulfur dioxide and halogen. The resulting compounds contain the said elements in the form of sulfohalide groups. The kind of compounds obtained and the number of sulfohalide groups depend on the nature of the initial material and on the manner in which the action of sulfur dioxide and halogen is carried out.

In the case of aliphatic hydrocarbons, the substances resulting from the treatment with sulfur dioxide and halogen are in most cases mixtures which contain unchanged starting material, and various sulfohalides, viz. products containing one sulfohalide group and others containing a plurality of such groups. These various sulfohalides are either employed as such or converted into sulfonic acids or their salts by hydrolysis. In view of the fact that the properties of the sulfohalides as well as of the hydrolyzed products vary frequently due to the position and the number of sulfohalide groups present therein, it is often desirable to separate the products from each other and in cases in which they contain unchanged initial material, and to separate it from the sulfohalides and to recover the same.

Particularly in the production of sulfonic acids from aliphatic hydrocarbons containing from between 12 to 16 or 18 carbon atoms by the treatment with sulfur dioxide and halogen and hydrolysis of the resulting sulfohalides it is necessary to remove unchanged hydrocarbons in order to avoid the formation of emulsions in consequence of the capillary activity of the sulfonic acids produced by the saponification of the sulfohalides with alkaline substances.

It is an object of the present invention to separate unchanged initial material from mixtures obtained by acting with sulfur dioxide and halogen on aliphatic hydrocarbons especially such containing from 12 to 18 carbon atoms.

It is a further object of our invention to separate from each other products having a higher content of sulfohalide groups from products containing less such groups.

The aim of this invention is reached by treating the starting mixtures with liquefied sulfur dioxide. The hydrocarbons serving as starting material for the treatment with sulfur dioxide and halogen are almost or entirely insoluble in liquid sulfur dioxide whereas the sulfohalides are more or less soluble therein. The solubility of

the sulfohalides in the liquid sulfur dioxide increases with the number of sulfohalide groups.

For example, a mixture obtained by acting with sulfur dioxide and chlorine on high-boiling liquid aliphatic hydrocarbons is stirred with liquefied sulfur dioxide whether at ordinary or even elevated temperature under pressure, or at a low temperature at its boiling point under atmospheric pressure or below. After standing for some time two layers are formed which may be easily separated from each other.

The separating action of liquefied sulfur dioxide, upon which the present process is based, is the better the lower is the temperature of working. Therefore, the process is advantageously carried out at relatively low temperature. Care must be taken, however, to choose the temperature not too low since the hydrocarbons used for the treatment with sulfur dioxide and halogen which accompany the resulting sulfohalides, frequently tend to become semi-solid or solid on cooling. This is particularly the case if higher molecular paraffin hydrocarbons are employed as starting material. In such cases the upper layer formed by the treatment with sulfur dioxide becomes a semi-solid mass which is difficult to work up further. If the process is performed, however, at higher temperature, in order to avoid such solidification, namely above the pourpoint of the hydrocarbons, the separating action of the liquefied sulfur dioxide becomes less satisfactory. In such cases the process can, nevertheless, be carried out to satisfaction if the treatment with the liquid sulfur dioxide is repeated once or several times.

Such repeated treatment can be avoided, however, by carrying out the process in the following manner, which may be called a two-stage process. In a first stage, the initial mixture is treated with liquid sulfur dioxide at a temperature above the pourpoint of the unchanged hydrocarbons, and the resulting two layers are separated from each other. In a second stage, the bottom layer which contains the main quantity of sulfohalides is then cooled for itself or with an added amount of sulfur dioxide until two layers are again formed which are also separated from each other. By working in this manner, the solidification of the hydrocarbons is avoided, while, at the same time, the sulfur dioxide extract is enriched in sulfohalides. In order to cool the bottom layer obtained in the first stage the usual methods may be employed but advantageously the cooling is effected internally by allowing the liquefied sulfur dioxide to vaporize

to such an extent that the desired temperature is reached. For this purpose a corresponding excess of liquid sulfur dioxide is employed so that after the vaporization of the part effecting the cooling sufficient sulfur dioxide remains dissolved behind to keep the sulfohalides. If necessary, the second stage may be repeated once or several times.

A particularly advantageous manner of carrying out the process consists in performing it continuously in a counter current by employing a column with fillers. This method is of particular value in cases in which the starting mixture contains appreciable amounts of unchanged hydrocarbons, as is the case if the treatment of the hydrocarbons, with sulfur dioxide and halogen is only carried on to such an extent that about half or less thereof is converted into sulfohalides.

Further particulars of our invention will appear hereinafter in the following Examples which illustrate the invention which is, however, not limited thereto. The parts are by weight.

Example 1

100 parts of a product obtained by acting with sulfur dioxide and chlorine on a mixture of aliphatic hydrocarbons, boiling between 240 and 360° C which have been produced by the catalytic hydrogenation of carbon monoxide, and containing as an average 4.87 per cent of sulfur, 7.30 per cent of chlorine, whereof 5.54 per cent are saponifiable, are stirred for some time while adding 300 parts of liquid sulfur dioxide. After standing for a short time two layers are formed. The bottom layer is a completely clear solution which contains the sulfochloride, whereas the hydrocarbons separate above it as an undissolved semisolid mass. By evaporating the sulfur dioxide which may be reliquefied and used again, a product is obtained which contains 12.40 per cent of saponifiable chlorine and which when saponified yields a product possessing high foaming power and giving with water a clear solution.

Example 2

200 parts of a reaction product obtained in a manner analogous to that described in Example 1 which contains 11.09 per cent of sulfur, 15.60 per cent of total chlorine and 13.40 per cent of saponifiable chlorine, are stirred with 400 parts of benzene, a sludgy dark-colored bottom layer being formed which is separated, whereafter the benzene is completely removed by distillation. The residue still contains 11.72 per cent of saponifiable chlorine. 200 parts of the product thus purified are then stirred with 450 parts of liquid sulfur dioxide, the mixture being then further treated as in the foregoing Example. There are obtained 25 parts of hydrocarbons and 174 parts of a sulfochloride, the content of saponifiable chlorine of which is 13.14 per cent.

The process according to the present invention may also be applied to a product containing sulfur, oxygen and chlorine obtained by acting with sulfur dioxide and chlorine on kerosene.

Example 3

2000 parts of a mixture consisting of about equal parts of sulfohalides and neutral hydrocarbons which is obtained by acting on a mixture of liquid hydrocarbons having an average molecular weight of 210 with sulfur dioxide and chlorine, are mixed in a closed vessel with the double amount by weight of liquid sulfur dioxide. The mixture is stirred at 15° C for some time and then allowed to stand until the formation of two layers is completed. The upper layer consists of 1250 parts. It contains 195 parts of sulfur dioxide, 211 parts of sulfohalide and 844 parts of unchanged hydrocarbons, corresponding to 1055 parts of a 20 per cent solution of sulfohalide in unchanged hydrocarbons. The amount of sulfohalide corresponds to 20 per cent, the amount of unchanged hydrocarbons to 80 per cent of the originally present quantity. The bottom layer consists of 4065 parts, namely 3205 parts of sulfur dioxide, 172 parts of unchanged hydrocarbons and 688 parts of sulfochloride corresponding to 860 parts of a 20 per cent solution of hydrocarbons in sulfochloride. After having separated the two layers, 3 per cent of the sulfur dioxide of the bottom layer are allowed to vaporize. The bottom layer is cooled thereby to 10° below zero C and two layers are again formed. In spite of the remarkable cooling and the high content of hydrocarbons, the upper layer does not solidify but remains liquid. After separating it and evaporating the sulfur dioxide contained therein it consists of 205 parts of a mixture containing 86 parts of sulfohalide and 119 parts of hydrocarbons. Calculated on the originally present amount this means 9 per cent of sulfohalide and 12 per cent of hydrocarbons. The bottom layer consists, after the vaporization of the sulfur dioxide, of 655 parts, namely 589 parts of sulfohalide and 66 parts of hydrocarbons. This layer consists consequently of a 10 per cent solution of hydrocarbons in sulfohalide; calculated on the originally present amount it contains 59 per cent of sulfohalide and 7 per cent of hydrocarbons.

The upper layer from the first stage is preferably used once more for the treatment with halogen and sulfur dioxide. The upper layer of the second stage is mixed with fresh initial mixture and simultaneously with it subjected to the separation according to this invention.

FRIEDRICH ASINGER.
RODERICH GRAF.
PAUL HEROLD.
CARL PLATZ.
WALTER SCHMIDT.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF HYDROPHILIC POLYMERIZATION PRODUCTS OF THE SUPERPOLYAMIDE TYPE

Max Hagedorn, Dessau, Germany; vested in the Alien Property Custodian

No Drawing. Application filed September 5, 1940

This invention relates to the manufacture of hydrophilic polymerization products of the superpolyamide type, said products being swellable in water and capable of being rendered water-soluble by application of heat.

The polymers known under the term superpolyamide up to now are manufactured by the condensation of monoaminocarboxylic acids or by reacting together diamines and dicarboxylic acids until condensation occurs. These products have chiefly been investigated with a view to obtain good thread- and film-forming qualities and as little water sensitivity as possible. The said products show in their chemical structure a certain similarity with the natural polypeptides and protein compounds, whereas their physical qualities differ largely from those of the said natural compounds.

It is an object of the present invention to change the structure of the synthetic linear high-polymers of the superpolyamide type in a sense to render them more similar to the aforesaid natural products.

A further object of this invention is to obtain superpolyamide condensation products which in their behavior towards water approach the physical characteristics typical for gelatin and glue.

These and other objects will become apparent from the following detailed specification.

According to this invention hydrophilic linear condensation products of the superpolyamide type are produced by heating a hydrohalide of an ω -amino carboxylic acid with at most three carbon atoms between the amino- and the carboxyl group with polyamide forming substances until condensation occurs. The products of this condensation or polymerization process are swellable in water and are easily rendered water-soluble by raising the temperature.

It has already been proposed to use the hydrohalides of short-chain amino carboxylic acids and their derivatives in the manufacture of polyamides. In this case they serve as catalysts to introduce or to promote the condensation of the chain units from which the superpolyamides are built up. In view of this purpose only quite small quantities of them were added to the reaction mixture and in order to exclude any undesired influence on the quality of the polymerization product, methods were taken to prevent the short-chain amino carboxylic acid unites to enter into the resulting superpolyamide. If, however, the hydrohalides of the amino carboxylic acids with at most three carbon atoms between the amino and the carboxyl group are applied in a quantity

of at least 10% or advantageously 20% or more than the quantities of the resulting superpolyamides are changed fundamentally. Depending on the amount of hydrohalide applied the reaction products are swellable or colloiddally soluble in water, whereas the aqueous solution at elevated temperatures constitutes a sol. It is changed into a gel on cooling.

The essential feature of our new process is the condensation of a short-chain ϵ -amino carboxylic acid with at most three carbon atoms with a long-chain polyamide forming substance.

As the short-chain component the hydrohalides of the lower aliphatic amino carboxylic acids, such as ϵ -amino carboxylic acids, amino acetic acids, α - or β -amino propionic acid, α -, β - or γ -amino butyric acid, their esters, amides, anilides etc. are to be used. It is recorded to apply the hydrochlorides of the methyl ethyl esters of the aforesaid amino carboxylic acids, since these are easily obtainable and most resistant to heat. Furthermore also the hydrohalides of aromatic amino carboxylic acids may be used provided that the amino- and the carboxyl groups are separated by one, two or three carbon atoms as in the case of anthranilic acids.

As a long-chain component for our new process all polyamide forming substances known in the prior art may be used. By way of example be mentioned ϵ -amino valeric acid, ϵ -amino capronic acid and their higher homologues either in the form of their free acids or their condensable derivatives, such as lactams, esters, acid amides, acid chlorides and the like, whereby it is understood that these reaction components may contain aliphatic or aromatic substituents. Interpolymers, such as they are for instance described in the copending U. S. Patent application Ser. No. 323,512, filed March 12, 1940, may be applied with advantage.

Instead of the ω -amino carboxylic acids the long-chain component of our new process may be a mixture of the long-chain dicarboxylic acids and long-chain polymethylene-diamines either in the form of the said compounds themselves, their neutral salts or their condensable derivatives. The diamines shall contain at least five, the dicarboxylic acids at least six carbon atoms between the amino groups and the carboxyl groups respectively. They too may contain aliphatic or aromatic substituents.

The characteristics of the condensation products as to the melting point, solubility etc. may for instance be varied by condensing mixtures of long-chain and short-chain units provided that

the percentage of the short-chain units in comparison to the long-chain units amounts to 10%. Under the same provision also other aliphatic or aromatic condensable substances may be added as well as such compounds which do not enter the mixed condensate, but merely act as softeners. It is obvious that it lies within the scope of my invention to apply mixtures of several components. Thus it is not indispensable to combine at least one long-chain component with the single short-chain component.

The condensation of the long-chain and the short-chain components is carried on in an indifferent atmosphere free from oxygen at temperatures between 150 and 250° C, advantageously 180 and 220° C in the melt. An indifferent medium may be present, whereas the addition of a special catalyst may in general be dispensed with. When the reaction is finished, the toughly viscous melt coagulates to a hard transparent or translucent resin when cooled.

The new superpolyamide products made according to the present invention are not only water-soluble at elevated temperature, but can easily be dissolved in mixtures of water with organic hydrophilic solvents, such as methanol, acetic acid etc.

My new superpolyamides are most useful as textile assistance, for instance thickening agents for printing pastes, sizing etc.

New to the behavior towards water they may be applied as coatings or panes of glass or translucent plastics, where humidity on that material must be absorbed. Since the new superpolyamides are in many respects resembling gelatin, they may be used in the photographic industry for all purposes in the manufacture of light sensitive materials in the form of plates, films, papers, where up to now gelatin is used as a substitute for gelatin, glue and aluminium. They are suitable for instance as a carrier for light sensitive substances such as dichromates, iron salts, silver halides, dye-azo-compounds. Furthermore the polyamides may be applied to form non-curling antihalo (antistatic) filter layers and protective coatings on photographic films or papers. The usual additions, such as stabilizers, matting substances, color formers, coupling components and glycerole may be added to the polyamides for the same purposes and with the same effect as gelatin. If desired, the aforesaid photographic layers may be prepared not entirely from polyamide, but from a mixture of polyamides with gelatin. The melting point, the solubility and the other physical qualities of these mixtures may be adjusted by varying the relative proportions of both substances.

Example I

120 grams ϵ -caprolactam are thoroly mixed with 30 grams glycollethylester hydrochloride and heated at 194–198° C during 20 hours in a carbon dioxide atmosphere after careful displacement of the air by carbodioxide. The main portion of the gaseous reaction products which escape is ethylalcohol. 125 grams of the solidified and pulverized reaction product are thoroly extracted with acetone and yield 90 grams of a red-brown dry powder. This is insoluble in cold water after a short treatment with cold water for the removal of the coloring water-soluble impurities, it dissolves, however, into a clear solution in hot water which solidifies after cooling into a deep-red, soft jelly. This jelly dries into a

clear film. It is reversibly precipitated by electrolytes and irreversibly by alkalies.

If the proportion lactam: glycolle is reduced from 4:1 to 3:1, the solubility in water is increased until the aqueous solution at a ratio 7:3 solidifies very incompletely when cooled down. To increase the proportion of the long component, on the other hand, reduces rapidly the solubility also in hot water; at the ratio lactam: glycolle 9:1 the solubility in water has completely disappeared.

Example II

If the glycollethylester hydrochloride in Example I is replaced by glycollehydrochloride and condensed at 240° C for 5 hours, a high polymeric reaction product of similar properties is obtained, which solidifies after purification with acetone (by extraction or precipitation from the hot aqueous solution) into a jelly from the hot aqueous solution. After drying it yields clear films insoluble in NH_3 (ammonia).

Example III

140 grams ϵ -caprolactam and 60 grams anthranilic acid ethylester hydrochloride are heated at 230° C for 16 hours under the same precautions as in Example I. The reaction product is a feebly yellow resin of medium hardness. The solution in water solidifies into a white mass having the consistence of curd. If the finely distributed reaction product is further very well dispersed in water, the centrifuged product gives with hot water again a clear solution which, however, solidifies into an opaque gel. The film thus obtained by drying is very feebly turbid, otherwise colorless.

If the ratio lactam: anthranilic acid is shifted from 7:3 over 6:4 to 5:5, the solubility in hot water remains intact, the capability of solidification, however, decreases rapidly. At a ratio 6:4 only a strong increase of viscosity occurs in the cold and at an even ratio of the components in the reaction the reaction product is clearly soluble in water, even in the cold.

Example IV

65 grams ϵ -caprolactam and 35 grams anthranilic acid hydrochloride are heated at 200–205° C for 24 hours under carbon dioxide. The yellow-green solid resin dissolves milkily in hot water and solidifies into a smear when cooled down. The increase of the portion of anthranilic acid hydrochloride in the reaction causes clear solubility of the polymeric reaction product in hot water. Such solutions, however, do not solidify any more when cooled down.

Example V

The reaction products as obtained according to Example IV from 80 grams ϵ -caprolactam and

- (a) 15 grams anthranilic acid ethylester hydrochloride + 5 grams glycollethylester hydrochloride,
- (b) 10 grams anthranilic acid ethylester hydrochloride + 10 grams glycollethylester hydrochloride,
- (c) 5 grams anthranilic acid ethylester hydrochloride + 15 grams glycollethylester hydrochloride

show generally the properties which are to be expected from their chemical constitution. The somewhat turbid, dark red solution of (a) in hot water solidifies into a yellow curd, the also feebly

turbid hot solution of (b) solidifies in the cold into a light brown smear. The reaction (c) behaves like (b), but the hot solution is completely clear.

Example VI

300 grams ϵ -caprolactam are thoroly mixed with 80 grams anthranilic acid and 20 grams glyccolylester hydrochloride and heated

under carbondioxide at 200° C for 8 hours, then at 120° C for 5 hours and finally again at 200° C for further 6 hours. The reddish, slightly sticky resin dissolves in hot water into a feebly turbid solution which solidifies after cooling into a soft paste, if a 10% solution is used as starting material.

MAX HAGEDORN.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF HYDROPHILIC POLYMERIZATION PRODUCTS OF THE SUPERPOLYAMIDE TYPE

Max Hagedorn, Dessau, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed September 5, 1940

This invention relates to the manufacture of hydrophilic synthetic linear condensation products of the superpolyamide type.

In my copending U. S. patent application Ser. No. ----- (corresponding to German patent application I. 65 184 IVd/12o, filed July 18, 1939) it has been shown that by condensation of ϵ -amino carboxylic acids with at least 4 carbon atoms between the amino- and the carboxyl groups with the hydrohalides of ϵ -amino carboxylic acids with the mentioned 3 carbon atoms between the amino- and the carboxyl groups hydrophilic super polyamides are obtained which are swellable or colloiddally soluble in water and assume the state of sole in an aqueous solution at elevated temperature, but become a gel on cooling.

Example

70 grams hexamethylene diammonium sebacate (2 mols) are thoroly mixed with 30 grams glycollethylester hydrochloride and heated after careful displacement of the air by carbon-dioxide in a carbondioxide atmosphere at 190-200°C for 17 hours. The clear melt solidifies after cooling into a red-brown resin. In the heat it is clearly soluble in water with dark red color. The solution solidifies into a clear paste after cooling. This highpolymeric condensation product is suitable as textile auxiliary agent, as diluent for printing inks and similar purposes.

MAX HAGEDORN.

ALIEN PROPERTY CUSTODIAN

CONVERSION PRODUCTS OF RUBBER

August Amann and Arthur Greth, Wiesbaden,
Germany; vested in the Alien Property Custodian

No Drawing. Application filed September 14, 1940

This invention is an improvement over Patent Number 2,200,715 and differs therefrom in the respects hereinafter indicated.

It has now been found that the conversion reaction of the rubber can be furthermore improved by replacing the isomerizing acids, which are not reactive to phenol, by their anhydrides. By doing this the decomposition reactions are almost completely eliminated, the resulting conversion products are more uniform and of improved quality. It has also been found that the acid anhydrides convert the rubber into a product which is soluble in linseed, chinawood or other varnish oils within a shorter time as the corresponding acids. It is also an essential advantage that the acid anhydrides, which are to be used, are less corrosive to the kettle material as for example iron etc., so that on the one side the reaction-rawproduct is obtained in a pure form and on the other side it is easier to supply suitable kettles.

Suitable acid anhydride are the anhydrides of the phosphoric and before all phosphorpentoxide. However also the anhydrides of the acids mentioned in the main patent are suitable f. i. the anhydrides of boric acid, trichlor-acetic acid and

the like. The amount of anhydride to be used corresponds the the amounts given in the main patent. The rubber conversion product is isolated from the reaction rawmaterial in the same way as described in the main patent or in the first amendment.

The process may be effected under pressure at temperatures above the boiling point of the phenol.

Example

570 parts of phenol, 375 parts of crepe rubber and 24.5 parts of phosphorpentoxide are heated for 4-6 hours to 170° at atmospheric pressure. After this time the conversion of the rubber is completed and the resinous product freed from the phenol by repeated precipitation from its toluol solution with alcohol. The purified product is soluble in hydrocarbons, linseed oil, china wood oil etc.

The conversion reaction can be completed within 1-1½ hours by applying pressure, the product possesses excellent varnish properties.

AUGUST AMANN.
ARTHUR GRETH.

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ALIEN PROPERTY CUSTODIAN

PROCESS OF PURIFYING CONVERSION PRODUCTS OF RUBBER

August Amann and Arthur Greth, Wiesbaden,
Germany; vested in the Alien Property Custodian

No Drawing. Application filed September 14, 1940

This invention relates to the purification of the raw isomerization products produced by the process of Patent Number 2,200,715 and of our concurrently filed copending application involving heating together rubber, phenol and acidic agents at normal or superatmospheric pressure.

It has been found that the crude rubber conversion product can be freed from the phenol in a technically easier and more commercial way by first dissolving it in an aromatic or aliphatic hydrocarbon or a mixture of both and successive washing of this solution with water and aqueous phenol. It has been found that two or three washings reduce the phenol content of the rubber conversion product so far, that the last traces can be easily removed by a simple steam distillation.

As to the aliphatic or aromatic hydrocarbons which are to be used as solvents for the rubber conversion product, it is advisable to use in first line those whose solvent action on phenol is less than that of water or aqueous phenol. It is therefore advisable to use preferably aliphatic hydrocarbons or aromatics with the addition of more or less aliphatic hydrocarbons. It is also advisable to use hydrocarbons which are generally used as lacquer varnish solvents, e. g. mineral spirits, white spirit, toluene, xylene, decalin etc, since such purified solutions can be used directly for the manufacture of coating materials.

The aqueous phenol, which is used for the washing of the rawproduct, shall contain such much water, that the phenol does not crystallize at room temperature. The water content shall be about 25% of the phenol-water mixture, however it can be also lower or higher without loosing the washing reaction. However it has been found, that the best separation the rubber conversion product solvent layer and the phenol-water layer is obtained fastest and best by using the above proportion of phenol : water in the washliquor. The separated phenol-water layer can be repeatedly used for the washing after dilution with water or crystallisation of the phenol.

After one or two washings with aqueous phenol the phenol-content of the rubber conversion prod-

uct is so low that the last traces can be easily removed by distillation after addition of a small amount of water.

The resulting solution of the rubber conversion product can be used for the preparation of coating compositions as it is or after addition of suitable solvents. It is compatible with gums, synthetic resins, celluloseesters, plasticizers, drying or nondrying vegetable oils as e. g. linseed, china-wood, castor oil and other rawmaterials, used in the coating industry. The rubber conversion product can be obtained also in a flaky-pulverized state by precipitation from its solution with a nonsolvent for the rubber conversion product.

Example

800 parts of the rubber conversion product, prepared by heating under pressure 50 parts of pale crepe rubber and 100 parts of phenol to 210° are dissolved in 1200 parts of mineral spirits to a 40% solution. 200-175 parts of water are added in order to liquify the crystallized phenol. After the separation of the two layers, the phenol solution, containing 9-10% of the phenol of the rawproduct, is separated from the benzine solution. By using more water or by trying to remove also the last traces of phenol from the benzine solution, emulsions are formed, which cannot easily be separated. Therefore the further purification is carried out with a phenol-water mixture, which surprisingly gives a fast and clean separation of the two layers. The benzine solution, 1740 parts, resulting after the first treatment with water is washed twice with each 445 parts of 75% aqueous phenol, by which the phenol content is reduced from 16-17% to 3-4%. This remaining phenol is easily removed by distillation at atmospheric or reduced pressure after addition of some water. According to the amount benzine distilled off, solutions of the rubber conversion products with various percentages of solids are obtained, which can be used as they are or diluted with other lacquer solvents.

AUGUST AMANN.
ARTHUR GRETH.

THE HISTORY OF THE

REIGN OF

CHARLES THE FIRST

BY

JOHN BURNET, BISHOP OF SALISBURY

IN TWO VOLUMES.

LONDON, Printed by J. Streater, at the Black-Swan in St. Dunstons Church, in Fleet-Street, 1679.

THE HISTORY OF THE

REIGN OF

CHARLES THE FIRST

BY

ALIEN PROPERTY CUSTODIAN

PREPARATION OF ALDEHYDES

Hans-Georg Trieschmann, Erich Jutz, and Franz Reicheneder, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed September 26, 1940

The present invention relates to the preparation of aldehydes.

The catalytic hydrogenation of alcohols of the acetylene series, e. g. of propargyl alcohol and its higher homologues or butine-2-diol-1.4 and its higher homologues, ordinarily leads to the formation of the corresponding alcohols of the paraffin and olefine series. Thus, for example, if butine-2-diol-1.4 is led with hydrogen of high pressure over a highly active hydrogenation catalyst, butanediol-1.4 or butanol is formed. When carrying out this reaction in the presence of a catalyst of low activity or under conditions which serve to reduce the activity of the catalyst, butene-2-diol-1.4 is the main reaction product.

We have found that aliphatic aldehydes may be prepared in good yields from alcohols of the acetylene series (alkinols) which correspond to the general formula $R-C\equiv C-CH_2OH$, wherein R represents a hydrocarbon radical, e. g. methyl or a higher alkyl radical, or the radical of a hydroxy-substituted hydrocarbon, as for example the radicals $-CH_2OH$ or $-CH_2CH_2-OH$. Our method consists in treating these alcohols with hydrogen in the presence of a hydrogenation catalyst under acid conditions.

In one method of carrying out our invention, the alkinol is passed together with hydrogen over a hydrogenation catalyst precipitated on an acid carrier, e. g. silicic acid gel. This method is most suitably carried out in the vapor phase. Especially high yields of aldehydes are obtained when using hydrogenation catalysts of low activity which promote only the addition of one molecular proportion of hydrogen to one molecular proportion of the alkinol. Such catalysts include finely divided metallic palladium, in particular palladium prepared by the reduction of palladium chloride or nitrate, or finely divided iron, as for example Raney-iron, furthermore nickel catalysts the activity of which has been reduced by poisoning, or mixtures of these catalysts, e. g. mixtures of palladium and iron.

Instead of using catalysts applied to acid carriers, there may be used catalysts which contain small amounts of acids originating from the catalyst preparation or to which small amounts of free acid have been added. In this case, there may be used other carriers, e. g. pumice stone or kieselguhr.

There is also the process of carrying out our invention in the liquid phase by allowing hydrogen to act on a mixture of liquid alkinol and a hydrogenation catalyst. In the liquid phase process the catalysts described above may also be utilized. It is also possible to use catalyst

compositions of non-acid character, provided that the reaction liquid has been acidified. Preferably the pH-value of the solution is within the range of between 2 and 6.

In general, the optimum temperature lies between 50 and 200° C. From 50 to 1000 grams of the vaporized alkinol may be passed per hour through 1 liter of the catalyst chamber. There may be used inert diluent gases or vapors or, when working in the liquid phase, inert diluent liquids wherein the alkinols are soluble. We prefer to carry out the reaction at normal pressure, though super-atmospheric pressure, e. g. pressures up to 10 or 30 atmospheres, may be used.

The following examples illustrate several ways in which the principle of our invention may be applied, but are not to be construed as limiting the invention.

Example 1

Palladium deposited on an acid carrier is used as the catalyst. It is prepared in the following manner: 5 grams of palladium chloride are dissolved in 200 grams of water, and the solution is thoroughly mixed with kieselguhr, containing about 3 per cent of iron and 1.7 per cent of SO_4 . The mixture is dried, and the powder obtained pressed into pills. The pills are reduced in a current of hydrogen at 200° C.

50 grams of a mixture consisting of 35 grams of propargyl alcohol and 15 parts of water per hour are vaporized at 150° C. The vapors are admixed with 40 liters of hydrogen and led over 100 cubic centimeters of the catalyst at 105° C. The vapors emerging from the catalyst are condensed. The aldehyde formed is separated from water and small amounts of allyl alcohol and propargyl alcohol by fractional distillation. 295 grams of propion aldehyde are thus obtained from 500 grams of the propargyl alcohol-water mixture. The yield exceeds 80 per cent of the theoretical yield.

Example 2

A 35 per cent aqueous solution of butine-2-diol-1.4 is heated to 95° C in a vessel charged with pumice stone. 60 grams of the preheated mixture are led per hour together with 30 liters of hydrogen over 100 cubic centimeters of the catalyst described in Example 1 at from 100 to 110° C. From 1000 grams of the butinediol solution there are obtained 250 grams of gamma-hydroxy butyraldehyde.

HANS-GEORG TRIESCHMANN.
ERICH JUTZ.
FRANZ REICHENEDER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR MANUFACTURING AFTER-CHLORINATED POLYVINYL CHLORIDE

Ernst Hanschke, Bitterfeld, Germany; vested in the Alien Property Custodian

No Drawing. Application filed September 27, 1940

The present invention relates to an improved process for manufacturing after-chlorinated polyvinyl chloride.

According to the process described in U. S. Patent No. 1,982,765 polyvinyl chloride is chlorinated by passing chlorine through an organic liquid such as carbon tetrachloride or tetrachloroethane in which the polyvinyl chloride is suspended.

Apart from the fact that by this method of working the chlorination occurs rather slowly and a multiple of the quantity of chlorine which is theoretically required escapes unconsumed and must be recovered, it is necessary to control continuously by taking test portions whether the desired chlorination degree has been attained. Moreover, care must be taken that the highest temperatures applied do not exceed the boiling point of the solvent used.

Now, I have found that this chlorination of polyvinyl chloride may be essentially simplified by performing it in the presence of an organic solvent, preferably a chlorinated aliphatic hydrocarbon, in a closed vessel under pressure. By addition of the quantity of chlorine necessary for the reaction temperature and cooling, if desired, when the chlorination has started, in order to remove an excess of reaction heat there is obtained after a short time and in a single manner a final product of definite properties, especially of a definite solubility. A further advantage resides in the fact that as suspending agent for the parent material there may also be used chlorinated hydrocarbons of low boiling point as, for instance, chloroform, from which the final product may be separated completely, for instance, by causing the reaction mixture to run into boiling water. Last not least, a smaller quantity of the solvent is used in the new process.

The following examples serve to illustrate the invention, the parts being by weight:—

Example 1.—50 parts of polyvinyl chloride of the degree of polymerization $K=62.3$, 800 parts of carbon tetrachloride and 50 parts of chlorine are heated in a roller or rocking autoclave at about 80° C. to 90° C. until reaction sets in. By cooling the temperature is kept at 100° C. to 110° C. After about 2 hours the chlorination has finished. The highest pressure amounts to about 9 to 10 atmospheres above atmospheric pressure. The reaction product which has separated contains 66.8 per cent. of chlorine. By suitably dosing the chlorine used, the contents of chlorine may be varied at will. The final products thus obtained

yield in tetrahydrofurfurane solutions of up to 15 per cent. strength.

Example 2.—22 parts of polyvinyl chloride of a K-value of 69.8, 300 parts of chloroform and 14 parts of chlorine are heated to 35° C. in a shaking autoclave. After the chlorination has set in, the vessel is cooled so that the temperature remains constantly at 90° C. to 100° C. The highest pressure during the reaction amounts to about 8 atmospheres above atmospheric pressure. After about 2 hours the chlorination has finished; the final product is separated by causing the reaction mixture to run into boiling water. The final product contains 63.2 per cent. of chlorine and yields in acetone solutions of 25 per cent. strength and in methylene chloride solutions of 20 per cent. strength.

Example 3.—A mixture of 30 parts of polyvinyl chloride of a K-value of 72.4, 300 parts of chloroform and 38 parts of chlorine yields after 2½ hours at a maximum temperature of 120° C. and a maximum pressure of 20 atmospheres a final product containing 67.3 per cent. of chlorine. It is insoluble in acetone, but yields in tetrahydrofurfurane clear solutions of 25 per cent. strength.

Example 4.—35 parts of polyvinyl chloride, 420 parts of tetrachlorethane and 35 parts of chlorine are heated in an autoclave to 85° C. In the course of 15 minutes the temperature rises to 90° C., care being taken by cooling that the temperature does not exceed 100° C. to 105° C. The maximum pressure amounts to 12 atmospheres above atmospheric pressure. Towards the end of the reaction the reacting liquor is heated to the said temperatures. After 1½ hours the reaction is finished. The final product contains 63.7 per cent. of chlorine and yields in acetone solutions of 25 per cent. strength and in methylenechloride solutions of 20 per cent. strength.

It is obvious that the invention is not limited to the foregoing examples or to the specific details given therein. Thus, for instance, other organic liquids which are inactive against chlorine may be used as suspending agents for the polyvinyl chloride under treatment. Although the reaction occurs very promptly it may be forwarded by addition of a chlorinating catalyst known per se in the art.

Furthermore, the process may be varied by introducing the desired amount of chlorine into the reaction vessel in stages so that always only limited quantities react with the polyvinyl chloride.

ERNST HANSCHKE.

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REPUBLIC OF THE UNITED STATES

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ALIEN PROPERTY CUSTODIAN

NITROGENOUS CONDENSATION PRODUCTS

Paul Schlack, Berlin-Treptow, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed September 27, 1940

This invention relates to new compositions of matter and more particularly to synthetic, nitrogenous, linear condensation products.

By action of diisocyanates on compounds with at least two functional groups reactive towards isocyanates such as oxy- or amino groups polyamide compounds are obtained which, when sufficiently polymerized yield valuable synthetic materials or synthetic resins. High molecular linear polyurethanes are obtained, when equivalent portions of diisocyanates are united with glycols, such as tetramethyleneglycol, decamethyleneglycol, xylyleneglycol or hydroquinone- $\beta\beta'$ -dioxidiethylether. Polymeric ureas are formed in a similar manner with diamines. Similar or identical compounds are also obtained, when diurethanes are caused to react with glycols or diamines (USA Patent Application Ser. No. 277,948, filed June 7, 1939).

These reactions are preferably carried out with urethane compounds in which the carbamic acid groups are esterified with an aromatic or enolic hydroxyl compound, especially with phenols (U. S. A. Patent application Ser. No.—, corresponding to the German patent application I.64 524 IVc/12 o, filed May 6, 1939).

This invention has as an object the preparation of new and valuable compositions of matter, particularly synthetic, fiber forming materials.

A further object is the preparation of filaments, fibers, ribbons, and foils from these materials.

A further object is to form these materials by casting, dye-casting, injection molding or pressing into useful articles.

A still further object is the manufacture of lacquers, coating compositions and impregnations for textile fabrics.

These and other objects will become apparent from the following description.

It has been found that various novel polyurethane compounds are obtained, which in their properties may deviate more or less from those hitherto described with regard to hardness, melting point, solubility and chemical reactivity, when diisocyanates and diurethanes (especially when containing aromatic or enolic hydroxyl compounds linked in esterified form) are caused to react with bifunctional hydroxyl- or sulfhydryl compounds, in which at least one of the functional groups shows alcoholic character, whereas the other may be present in the form of a carboxyl group, an amino group or a monosubstituted amino group. Furthermore the compounds must be chosen in such a way that at least one bi-

functional compound reacting in substantial, preferably stoichiometrical quantity contains preformed amide groups (carbonamide groups, urea groups, sulfamide groups, sulfonamide groups linked to carbonaceous radicals), whereby compounds containing urethane groups only are excepted. The amide groups may be built into open chains or may be constituents of heterocyclic rings being built into the chain. Moreover, they may not only be present in one of the two reactants, in the active (acylating) or in the passive (to be acylated) component, but simultaneously also in both of them. The new possibilities obtained hereby are various and a great variety is given in controlling the properties of polyamide compounds according to the intended use.

According to the present invention there are condensed diisocyanates or diurethanes with glycols, dimercaptans, amino alcohols, amino mercaptans, oxycarboxylic acids, mercapto carboxylic acids, of which components at least one contains preformed amide groups. Polyamide compounds are thus obtained, which show urethane- or thio-urethane groups besides the preformed amide groups introduced by the starting material. For each linkage they display at least one of these ester groups, when, as it is generally the rule, two homogeneous components are caused to react with each other.

In principle one may work with more than two components. Besides glycols, oxycarboxylic acids or amino oxy compounds containing already an amide group, for instance a carbonamide group, there may be present furthermore simple glycols, oxycarboxylic acids or amino alcohols without such groups in the reaction mixture.

It is also within the scope of this invention, when dicarboxylic acids, for instance adipic acid, oxodibutyric acid (German Patent application I.63 283, filed December 23, 1938) or diamines, such as hexamethylene diamine and $\gamma\gamma'$ -diamino dipropylether are present in part in the reaction mixture. Furthermore there may be added in part polyamide forming compounds, such as amino carboxylic acids or salts from diamines and dicarboxylic acids. Also these components or pair of substances may contain amide groups in the molecule (according to U. S. Patent application Ser. No.—, corresponding to the German Patent application I.64 579 IVD/12 o, filed May 11, 1939).

Besides the bifunctional components there may be added in minor quantities also polyfunctional compounds, for instance polycarboxylic acids with more than two carboxyl groups or their reactive

functional derivatives, furthermore, aminoxy-carboxylic acids. Finally substances may be added for regulating the chain length and influencing the electro-chemical character of the end-product, which under the given reaction conditions are capable to react on one side only, for instance monovalent alcohols or amines, such as dodecyl alcohol, octadecyl alcohol, cyclohexylamine, octodecyl amine, furthermore amino alcohols with tertiary amino groups or diamines with one tertiary amino group. Such substances may be added also during the condensation, if necessary, towards the end of the reaction. It is advantageous to work with two homogenous reactive components. Polymeric compounds of uniform or at least regular structure are then obtained, which for many purposes are more valuable than substances obtained by direct condensation of more than three components. In the latter case the course of reaction is very complicated, since the speed of reaction of the single components may vary considerably. Uniformly or regularly built substances differ more or less considerably in important properties, for instance melting point and solubility, from the chemically isomeric mixed-condensates obtained when a mixture of the final hydrolysis products or their derivatives, on which the polyamide in question seems to be based, is condensed.

Numerous methods may be employed for the synthesis of condensable components which are applicable according to the present invention. As far as the starting material for the production of isocyanates or diurethanes is concerned, the same diamino compounds with amide-like chain-interruption come into question as described in German Patent application I.64 527 IVc/12p, filed May 6, 1939 and U. S. Patent application Ser. No. -----, corresponding to the German Patent application I.64 579 IVd/12o, filed May 11, 1939.

The conversion of these diamines into diisocyanates is accomplished in the usual manner by action of the hydrochlorides on phosgen in an indifferent solvent which practically has so high a boiling point that the carbamic acid chlorides primary formed are decomposed by boiling. Also the urethanes, as far as they are not built up from a starting material containing urethane groups are manufactured in a known manner, i. e. by the action of the diamines or their salts on halogen formic esters, for instance chloroformic acid phenyl ester, or as far as the aryl ester is concerned by the action of the free amines on the diarylcarbonate, the latter being preferably employed in excess.

In as far as isocyanate compounds are employed it is useful to choose simple components, since only such substances can be purified by the inexpensive method of distillation. Isocyanates of more complicated constitution are best obtained and worked up in solution, whereby the contents of the solution may be easily found out by action of substances yielding insoluble precipitation, such as aromatic amines.

In what various ways the components may be changed within the scope of the present invention can be seen from the following table. The invention is not limited to the types mentioned therein and to the substances described in these examples. Generally speaking the present invention relates to the manufacture of polyamides with urethane groups from components which already possess, at least partly, preformed amide groups.

TABLE

BIFUNCTIONAL COMPOUNDS REACTIVE WITH DIISOCYANATES OR DIURETHANES

(I.) Glycols and diurethanes

(a.) Compounds with amide groups in open chain

(1.) $\text{HO}-(\text{CH}_2)_x-\text{NR}-\text{CO}(\text{A})-$

$\text{CO}-\text{NR}-(\text{CH}_2)_x-\text{OH}$

x =at least 2, practically 3 or more, A =bivalent organic radical, may be=O. $\text{R}=\text{H}$ or a monovalent, if necessary substituted hydrocarbon radical.

These compounds are obtained by the action of the dicarboxylic acids or their functional derivatives on amino alcohols, for instance oxalic acid, oxalic acid esters, adipic acid, adipic acid esters or adipic acid chloride. Suitable dicarboxylic acids are besides oxalic acid and adipic acid the following: malonic acid, glutaric acid, sebacic acid, oxodibutyric acid, oxalyl-bis-amino caproic acid, terephthalic acid, hexamethylene-bis-oxamic acid dialkyl ester.

(2.) Dimercaptanes according to formula 1 are obtained from the amino mercaptanes by acylation with dicarboxylic acids or from the alkyl amine halides, such as 3-chloropropylamine, and dicarboxylic acids with following exchange of halogen against sulfhydryl.

(3.) Glycols and dimercaptanes with urea- or thiourea radicals.

$\text{HO}-(\text{CH}_2)_x-\text{NR}-\text{CO}-\text{NR}-(\text{CH}_2)_x-\text{HO}$
(HS) (CS) (SH)

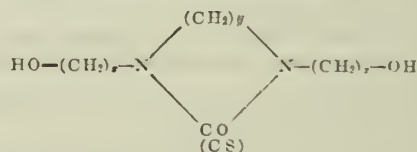
x =at least 3, 4 or more.

The compounds are obtained from the amino alcohols or amino mercaptanes by action of phosgen or carbonic esters or carbondisulfide or thiocarbonylchloride. The ureas are generally less valuable than the amides, since they have as a rule lower melting points. Instead of the simple compounds with phosgen or thiophosgen there may be placed an alkylene-bis-carbonyl group. It is possible, for instance, to combine amino alcohols or amino mercaptanes with a diurethane or with a diisocyanate, such as hexamethylene-diisocyanate. Components of considerably higher melting point are thus obtained.

As described above the mercaptanes may also be obtained by the way of alkylamine halides.

(b.) Glycols (dimercaptanes with amide groups in heterocyclic rings)

(1.) Cyclic ureas and thioureas.

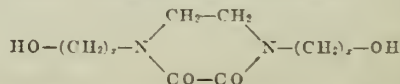


x =at least 2, y =2 or 3.

These compounds are obtained by the action of primary amino alcohols on alkylene chlorides and following ring formation with phosgen or thiophosgen.

Dimercaptanes are obtained in a similar manner by way of the corresponding halogen alkyl ethylene diamines.

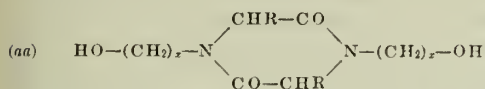
(2.) Cyclic amides of the oxalic acid.



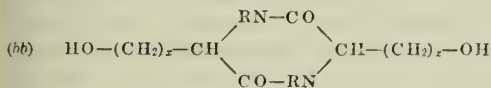
x =at least 2, preferably more than 3, obtained

by the action of dioxyalkyl ethylene diamines on oxalic acid diphenyl ester or other oxalic acid compounds.

(3.) 2,5-dioxopiperazine compounds.



=alkyl, $x=2$ or more, easily obtainable by reaction of the amino alcohols with the halides of fatty acids, esterification and cyclization of the amino esters or by the action of the amino alcohols on an aldehyde, especially formaldehyde and hydrocyanic acid, esterification of the nitrile and cyclization of the ester.

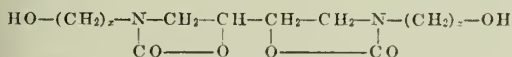


$x=2$ or more, obtainable from α -amino acids in the usual way.

Example.—Di- β -oxyethyl-diketopiperazine.

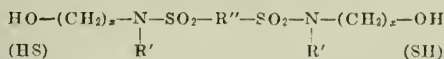
(4.) Glycols with oxazolrings.

$x=4$ or more.



It is obtained by condensation of excess amino alcohols with butadiene dioxide and following reaction with diphenylcarbonate.

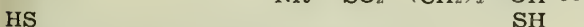
(5.) Glycols (mercaptanes) with sulfo groups.



R' =alkyl or substituted alkyl radical,

R'' =bivalent organic radical, for instance trimethylene or phenylene.

These glycols are obtained from bivalent sulfochlorides in a straight reaction, for instance by action of trimethylene disulfochloride or benzene disulfochloride on amino alcohols or amino mercaptanes. The mercapto group may also be introduced through ω -alkyl halide radicals. Ethane-disulfochloride cannot be used as component.



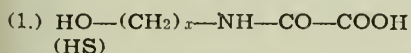
R' =alkyl or substituted alkyl radical,

R'' =bivalent organic radical,

x =two or more, preferably=3 or more.

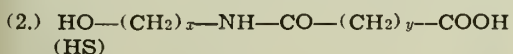
Best obtainable by action of halogen alkyl sulfochlorides on diamines, for instance ethylene diamine, symmetrical dimethyl ethylene diamine, hexamethylene diamine with following exchange of the halogen against OH for SH.

II. Oxy(mercapto)-carbonic acids



$x=2$, better 3 or more.

Action of the amino alcohols or amino mercaptanes on excess oxalic acid esters and saponification of the oxamide acid esters thus formed.

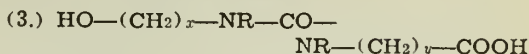


$x=2$, better 3 or more,

$y=1$ or 3, better 4 or more.

Obtainable by action of the amino alcohols on

excess dicarboxylic acid esters and saponification of the amide esters thus formed.



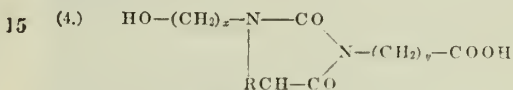
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(HS)

$x=2$, better 3 or more,

$y=3$ or more.

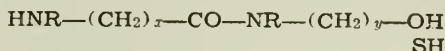
Such compounds are obtainable for instance by action of the urethane amino acids or urethane amino acid esters on amino alcohols or mercaptoalcohols, which, if necessary, are afterwards saponified.



$x=2$, better 3 or more,

20 y =at least 2, preferably 4 or more.

(III.) Aminoxy-(mercapto) compounds



x =at least 5,

25 $y=2$, preferably 3 or more.

Compounds of this kind are obtainable by a reaction of the amino carboxylic acid esters with excess amino alcohols or by the action of the amino acid chloride hydrochlorides on amino alcohols. Furthermore they can be obtained by coupling of the amino alcohols with formyl amino carboxylic acid chlorides and removing of the formyl group by boiling with alcohol containing sulfuric acid.

The afore-mentioned table is in no way exhaustive. It exhibits only the general types of compounds adapted for the present invention and shows furthermore by what general reactions they can be obtained.

If for instance in the table is stated, $x=2$, preferably 4 or more, it means, that with compounds of the type $x=2$ there are obtained polyamides which as a rule are not high polymeric or which possess moderate thermal resistance only. Components of the type=4 or more, however, yield more stable and more valuable compounds. The condensation degree of which may be increased considerably.

In the practical application of the reaction the components may be directly given together or melted together provided, the reaction is not too violent. If the latter is the case (with isocyanates) a solvent or diluent is necessary, which at the end of the starting reaction can be distilled off immediately. Hydrocarbons for instance and their halogen compounds are most suitable hereto, such as chloroform, tetrachloroethylene, benzene, chlorobenzene, o-dichlorobenzene, also ethers, such as dibutyl ether, dioxane, dimethyldioxane and stable esters, such as butyl propionate. Instead of the indifferent solvents or diluents or together with those there may be employed also dissolving compounds containing hydroxyl- or amide- or imide groups. These compounds do not yield substances which with isocyanates are stable at elevated temperatures. This are for instance phenols, such as phenol, m-cresol, xyleneol, p-tertiary butylphenol and especially phenols negatively substituted by halogen, such as p-chlorophenol or p-chloro m-cresol. Of the imide compounds there comes into question for instance carbazole.

The presence of phenols in the reaction mixture may influence the quality of the final product in a specifically optimal manner. Net-forma-

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tions, which for instance may occur in the presence of urea groups with H on the nitrogen atom, do not set in after addition of phenol, or at least to a much smaller degree. Solvents may naturally be employed, when a violent starting reaction is not to be expected, for instance, when the reaction products melt only at high temperature being near to decomposition.

It is practical, especially when the reaction temperature lies above 150° C, to cut off atmospheric oxygen, for instance by conducting a stream of nitrogen current over the reaction mixture. Generally speaking the polyurethane amides are less oxidizable than linear polyamides, which are obtained by condensation of carboxyl compounds with amines.

In order to work up the melt, liberated if necessary from the solvent by a vacuum distillation, it may be extruded through nozzles in the form of a bristle or ribbon, preferably while cooling with water, if one does not prefer to spin the filaments directly from the primary melt. If solvents being solid at room temperature, for instance p-chloro-m-cresol, are used the solidified melt may be disintegrated and the solvent be removed with a non-solvent for the polymer, such as methanol or acetone. The relatively low polymeric compounds thus obtained may be further condensed by reheating in the molten state, preferably in vacuo, until a certain viscosity is attained.

When recondensing the primary reaction products, it is often advantageous to add small amounts, $\frac{1}{300}$ – $\frac{1}{50}$ mol of a dicarboxylic acid, for instance adipic acid, sebacic acid, oxalyl-bis-amino caproic acid. (U. S. patent application Ser. No. —, corresponding to German patent application I.64 579 IVd/120, filed May 11, 1939). Such admixtures suitably dosed facilitate the formation of a higher polymerization degree, provided the reactive groups in the reaction product are not lost by oxidation or other side-reactions.

Polymers, which before recondensation are to be precipitated, are practically treated in the presence of a small amount of a phenol, in order to maintain the reactivity.

Finally the primary reaction products may be dissolved in a solvent not used during the condensation, such as formic acid or acetic acid, and may be precipitated again from this solution by adding non-solvents or by discharging them into non-solvents. By a suitable choice of the quantitative proportion of solvent and precipitant there may be accomplished simultaneously a purification or fractionation. The products according to the present invention are of wide use. Decidedly high polymeric compounds are valuable starting materials for formed structures. They may be worked up in the thermoplastic or plasticised state, from the melt or from solutions, for instance in phenols, formic acid, acetic acid, in some cases also alcohols into filaments, ribbons, bristles, foils, and films. Further they may be formed by casting, dye-casting, injection molding or pressing in any desirable manner. Substances of a medium polymerization degree are suitable for the manufacture of lacquers and coating compositions or for impregnation, especially of textiles. Water soluble products may be used as protective colloids. Generally speaking they may be employed as auxiliary agents in the different branches of the textile industry and also in the related branches of chemical technology, for instance in the paper- and leather industries.

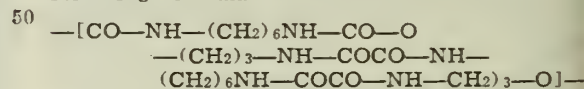
EXAMPLE I

To a solution of two mols 3-amino propanol in alcohol there is added, while cooling, one mol oxalic acid dimethyl ester in as little methanol as possible. The symmetrical di-3-oxy-propyl-oxamide (f. p. 160° C) is hereby formed in very good yield. To the diamide dissolved in m-cresol at elevated temperature there is given the corresponding amount of hexamethylene diisocyanate. The mixture is gradually heated up at 180° C, while stirring, and kept at this temperature for 3 hours, whereby atmospheric oxygen is excluded.

The solution after cooling is precipitated with dry acetone. The product which is thoroughly washed with acetone is remelted in a nitrogen atmosphere and heated up at 230° C for 3 hours under 1 mm pressure, whereby part of the cresol is distilled off. The polyurethane melts towards 195° C. The melt can be spun directly. A product being also spinnable is obtained, if the di-oxypropyl oxamide is suspended in benzene, part of the benzene for elimination of the last traces of humidity is distilled off and if the exactly calculated amount of hexamethylene diisocyanate in water-free benzene is added and the mixture boiled for 2 hours under reflux. The benzene is then distilled off and the residue still heated up at 240° C for 3 hours in vacuo of 1–2 mm.

EXAMPLE II

1 mol hexamethylene diamine is added to excess oxalic acid diethyl ester (4 mols in the same volume of alcohol). The hexamethylene-bis-oxamic acid ethyl ester (f. p. 80° C) is precipitated in colorless plates. 1 mol of it is dissolved in warm alcohol and there are added 2 mols of 3-amino propanol. The ω , ω' -di- γ -oxy-propylhexamethylene-bis-oxamide (f. p. at about 195°) thus obtained in good yield is heated with the equivalent amount of hexamethylene-bis-carbamic acid diphenyl ester at 160–180° C in a nitrogen atmosphere. After 3 hours the pressure is gradually reduced to 2 mm. and the temperature finally increased at 240° C. The temperature of 240° C is kept 2–3 hours. The polyurethane amide thus obtained probably of the following formula



can be spun into filaments directly from the melt.

EXAMPLE III

3-amino propanol hydrochloride is shaken for 6 hours with the calculated amount of ammonium chloride and potassium cyanate in the presence of ether thus forming 3-oxypropyl-sarcosine nitrile. This is saponified with methanolic hydrochloric acid into the methyl ester and the ester thus liberated is then heated at 160–170° C for about 4 hours in phenol. It is cyclized hereby to NN'-bis-3-oxypropyl-dioxypiperazine. This (1 mol) is dissolved in three parts of o-chloro phenol, traces of water are distilled off by adding a small amount of benzene. The exactly calculated amount of octamethylene diisocyanate (1 mol) dissolved in benzene is then added. After heating at 80° C for one hour the temperature is first raised to 150° C, whereby the main amount of benzene distills off, and finally to 200° C, where it is kept for 3 hours. The polyamide is then

precipitated by adding water-free acetone which contains 5% phenol.

By remelting of the product and heating in vacuo, if necessary by adding a small amount of dicarboxylic acids in quantities of for instance $\frac{1}{300}$ – $\frac{1}{50}$ mol calculated on the diisocyanate being used, the condensation product may be brought to still a higher polymerization degree. If the o-chlorophenol is replaced by the less acid phenol, the tendency for lower polymeric compounds prevails, because the o-chlorophenol is less reactive with isocyanates.

EXAMPLE IV

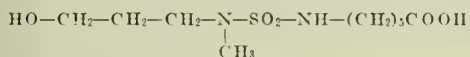
NN'-di-5-oxy-pentylurea obtained by action of 2 mols 1-amino-pentanol-5 on 1 mol diphenyl carbonate at 100° C is dissolved in dry dioxane in a pressure vessel and there is added to the solution the calculated amount of tetramethylene diisocyanate. After the reaction is over the vessel is sealed and heated at 240° C for 3 hours. The solvent is gradually blown off at this temperature and the product is heated finally still $1\frac{1}{2}$ hours in vacuo (2 mm) under a nitrogen current. The melt is then extruded in cold water through a slot. The polyamide is obtained in the form of a thick, elastic, very flexible ribbon.

EXAMPLE V

ϵ -bromo caproic acid chloride (obtained by action of the ϵ -bromo caproic acid on thionylchloride, the ϵ -bromo caproic acid being obtained from ϵ -amino caproic acid and nitrosylbromide) is coupled in alkaline solution with ϵ -amino caproic acid and the bromide is replaced by hydroxyl by boiling with potassiumformate in 70% alcohol. The ω -oxycapronyl caproic acid is united with the equivalent amount of tetramethylene diisocyanate in tetrachloroethylene. After the initial reaction is over, the mixture is boiled for one hour and the solvent distilled off. The residue is gradually heated until 190–200° C finally in vacuo (about 2 mm). After 5–6 hours the product is spinnable from the melt.

EXAMPLE VI

N-methyl-3-chloropropyl amine hydrochloride is converted with sulfurylchloride in carbon tetrachloride into the N-sulfo chloride and this is coupled with an alkaline solution of ϵ -amino caproic acid. The N- γ -chloro-propyl sulfamide-N'- ϵ -caproic acid is saponified by boiling with excess potassium formate in 70% alcohol. The hydroxy acid thus obtained of the formula



is caused to react with the equivalent amount of tetramethylene-bis-carbamic acid diphenyl ester by heating at 100–190° C finally in vacuo. The temperature is raised so that 180° C are reached within two hours. It is then heated another 3 hours at 180–190° C. By remelting of the reaction product liberated from the phenol by disintegrating in acetone the polymerization degree may be increased by further splitting off of phenol in vacuo.

EXAMPLE VII

1 mol trimethylene disulfochloride is coupled at 0° in aqueous solution with 3-amino propanol. The NN'-di- γ -oxypropyltrimethylene disulfamide thus precipitated is heated with tetramethylene-bis-carbamic acid diphenyl ester for one hour at 150° C, then gradually at 180° C under reduced pressure and finally at 220° C. A

tough resin is obtained which in solution, for instance glacial acetic acid, is useful for impregnating or seizing of textiles.

A product chemically very similar is obtained when 3-amino propanol in water is shaken with a solution of m-benzene disulfochloride in ether and the reaction product thus obtained is condensed with tetramethylene-bis-carbamic acid diphenyl ester.

EXAMPLE VIII

3-chloropropylamine is condensed in an alcoholic solution of methyl amine into di-(γ -amino-propyl) methylamine. The free amine is discharged into a 60° C hot solution of excess diphenylcarbonate in benzene. Hereby the di-N-propyl-methylamine-3-3'-carbamic acid diphenyl ester is obtained. By condensing the same for 4 hours with $\gamma\gamma'$ -dioxypopyl oxamide at 160–180° C in a nitrogen current a condensation product is obtained, which is easily soluble in acids and which precipitates high molecular compounds with acid groups, such as dyestuffs and tanning matter. By alkylation with dimethyl sulfate the tertiary amino groups may be converted into quaternary ones. The aqueous solution of the methylated products also precipitates dyestuffs and tanning matter.

EXAMPLE IX

The NN'-di- γ -oxypropyl-ethylenediamine obtained by condensation of ethylene bromide with excess 3-amino propanol is converted by means of thiophosgen into the cyclic thiourea. By the reaction of thiourea with a solution of the equivalent amount of hexamethylene diisocyanate in dioxane and boiling of the reaction mixture for 3 hours a polyurethane is obtained, which becomes water-soluble by a treatment with alkylating agents, such as dimethylsulfate, benzylchloride or chloroacetic diethylamide. The aqueous solution precipitates tanning matter and dyestuffs with acid groups. By an alkali treatment the alkylated product becomes again water-insoluble by splitting off the sulfur groups.

EXAMPLE X

3-amino propanol is acylated in aqueous 30% solution by shaking with terephthalic acid chloride in ether. The terephthaloyl-bis-aminopropanol (f. p. 187° C) thus obtained is condensed with the equimolecular amount of hexamethylene-bis-carbamic acid xylenyl ester (from hexamethylenediamine and the chloro formic acid ester of technical xylenol) in xylenol for 8 hours at 180–220° C and the polyurethane amide is finally precipitated with acetone. By remelting of the product purified with acetone and by an after-condensation shortly above the melting temperature during 4 hours at 2 mm the degree of polymerization is increased.

A similar product of lower melting point is obtained from adipinyl-bis-amino propanol (obtained from adipinylchloride and propanol amine, f. p. 128° C).

EXAMPLE XI

Naphthalene tetracarboxylic acid dianhydride is condensed in di-chlorobenzene with 2 mols 5-aminopentanol-1. The bis-NN'- ω -oxy-pentyl-naphthalene-tetracarboxylic acid diimide thus obtained is mixed with octamethylene-bis-carbamic-p-chlorophenyl ester (obtained from the diamine with chloro formic acid p-chloro phenyl ester) by adding of $\frac{1}{100}$ mol iso-octylphenol-lithium (calculated on the diimide). The mixture is first

heated for 1 hour at 150° C by adding of 2 parts of p-chlorophenol and then for 9 hours at 190–200° C. The mass solidified after cooling is then disintegrated and liberated from the p-chlorophenol by extraction with acetone. By remelting in vacuo the polymerization degree of the product may be increased.

EXAMPLE XII

3-amino propanol is shaken in benzene with ϵ -amino caproic acid chloride-hydrochloride (prepared from the amino acid according to the method of Emil Fischer). ϵ -amino-caproyl-3-aminopropanol is formed hereby in good yield. The amine freed from the hydrogen chloride is condensed with tetramethylene-bis-carbamic acid diphenyl ester by heating for 10 hours at 180–240° C, at the end under 2 mm. The polyamide thus formed is spinnable into filaments directly from the melt.

EXAMPLE XIII

1 mol 3-mercaptopropyl amine sodium is caused to react in alcoholic solution with $\frac{1}{2}$ mol oxalic acid diethyl ester. The dimercaptane isolated under exclusion of oxygen is heated at 180° C with hexamethylene-bis-carbamic acid diphenyl ester and is kept at this temperature for 10 hours. After cooling the melt is dissolved in formic acid and the polyamide precipitated as yellow powder by means of acetone.

EXAMPLE XIV

3-amino propyl mercaptane sodium is caused to react in alcoholic solution with excess oxalic acid diethyl ester. The 3-mercapto propyloxamide acid obtained by saponification with alkali is condensed by heating for 8 hours into a polyamide at 120–190° C with the equivalent amount of hexamethylene-bis-carbamic acid di-p-cresol ester.

EXAMPLE XV

2 mols of 5-amino phthalic acid are coupled in

alkaline solution with sebacic acid into sebacinyl-bis-5-amino phthalic acid. The acid is converted by boiling with chlorobenzene into the dianhydride and this is condensed with 2 mols 3-aminopropanol-1 at 100–170° C, preferably o-dichlorobenzene is used as diluent. The sebacinyl-bis-5-aminophthalic acid- γ -oxypropylimid thus obtained is heated with the equivalent amount of hexamethylene-bis-carbamic acid-p-chlorophenyl ester at 200–210° C. After heating for 3 hours the chlorophenol thus formed is distilled off in vacuo and the temperature is thus regulated that the mass remains melted. All together the mass is heated for 8 hours. The reaction product is dissolved in formic acid and precipitated with chlorobenzene. Well adhesive coatings are obtained.

Instead of the carbamic acid ester the corresponding diisocyanate may be employed. In this case o-dichlorobenzene is employed as diluent and the reaction temperature is kept below 100° C within the first hour. The mass is then boiled for 4 hours and the solvent distilled off. Also this product can be dissolved and reprecipitated from formic acid. By an after-condensation of the melt being liberated from solvents the polymerization degree may be increased.

A similar but higher melting product is obtained by employing adipinyl-bis-amino phthalic acid- γ -oxypropylimid instead of the sebacic acid compound.

EXAMPLE XVI

Lysine anhydride is converted into the dianhydride by means of chloro carbonic acid phenyl ester. 1 mol of it is heated for 2 hours at 180° C with 1 mol decamethyleneglycol. The phenol formed thereby is distilled off in vacuo. After further heating for 6 hours at 180–200° C a tough resin is obtained which solidifies after cooling into a hard mass.

PAUL SCHLACK.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREPARATION OF FATS AND OILS WHICH ARE SUITABLE FOR IN- JECTION

Felix Grandel, Emmerich/Rhein, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed October 9, 1940

This invention relates to a process for the preparation of fats and oils which are suitable for injection.

For the purpose of incorporating therapeutical remedies into the body by way of injection, disper-
sions, or solutions, or emulsions with an agent
are used, which consist of refined fats and oils.
More particularly raw fats and oils are concerned
in this regard, which are purified by way of re-
fining methods, for instance a method with a
caustic lye of soda. Crude oils and fats in the
condition, in which they are obtained from the
fatty or oily raw materials, are not suitable for
purposes of injection, because the accessory sub-
stances contained therein would bring about
phenomena of necrosis and encapsulations of fat
at the place of injection, or even a fat embolus.
Refined sesame oil, or olive oil are, for instance,
frequently used as oil solvents for therapeutical
remedies.

As long as it was only a question of preparing a
dispersing agent or a solvent, which is most read-
ily assimilated by the body, and is without any
biologicotherapeutical effects of its own, it was
sufficient to prepare neutral fatty agents perfectly
free of accessory substances, and as pure and col-
ourless as possible, from the raw fats and oils in
accordance with the well-known refining proc-
esses. If, however, the end aimed at was to pre-
serve the biologically efficient substances or the
agents enhousing the assimilative capacity of the
oils or fats, other manufacturing methods had to
be found, because by the processes of purification
hitherto used these valuable agents were either
destroyed or removed.

The resorption of fats and oils is favourably in-
fluenced by the phosphatides. If it is thus in-
tended to use the fats and oils as solvents, as dis-
persing agents or emulsifiers for therapeutical
preparations, it is advisable not to expel from
them those accessory substances, which are con-
tained in them and expedite their assimilative
force, as was done hitherto by the processes of re-
fining and bleaching, but to take care that as
great a fraction of them, as feasible, is preserved.

In the event that in view of the biological effect
of their accessory substances the oils or fats are
themselves intended to play the part of a remedial
agent, it will also not be possible any longer to
prepare injectable and assimilative fats and oils
under those methods of purification, as are al-
ready known, e. g. refining with alkaline sub-
stances, because these processes result in a con-
siderable destruction and removal of the biologi-

cally important admixtures from the raw fats
and oils.

When raw fats and oils are purified, frequently
a destruction of those accessory substances con-
tained in them, as are of biological and thera-
peutical importance, will take place, which de-
struction is either due to the prolonged heating
period at a raised temperature, when air is ad-
mitted at the same time, or to the refining agents,
such as alkaline substances, acids, solvents. In
addition, thereto the neutral fatty substance is,
moreover, attacked during this refining action to
a degree, which must not be underrated. As far
as a refining process with alkaline substances is
concerned, the therapeutically important acces-
sory substances of the fats and oils are, more-
over, adsorbed and absorbed by the stock of soap,
and thus separated, the great losses in neutral fat
sustained in consequence of this refining process
must also be considered, said losses being of par-
ticular importance, of the fats and oils concerned
are valuable and efficient under biological and
therapeutical aspects.

It has now been found—and this is the main ob-
ject of the present invention—that fats and oils,
which are suitable for injection and readily ab-
sorbed, can be prepared in a simple manner by
heating the raw fats and oils having a biologico-
therapeutical effect of their own, or not, in the
presence of an indifferent gas,—exposing them, if
desirable, only to an instantaneous heating ef-
fect,—and subsequently cooling them.

By way of this simple treatment the raw fats
and oils, either containing substances of their
own, or not, which are biologico-therapeutically
efficient, are rendered suitable for purposes of in-
jection, i. e. they are deprived of any irritative
effect, and will neither bring about an irritated
condition, nor any effect resulting in a shock, as
has been established by several hundreds of in-
jection tests on men and animals.

In order to carry the process into practice, the
type of apparatus used for instantaneous heating
(Pasteurization) of milk is particularly suitable.
Under the new process the substances detrimental
to injection are removed in an extremely unhurt-
ful manner, and without any considerable detri-
mental influence upon the other ballast sub-
stances,—whether with or without a biological or
therapeutical effect—which are important with
regard to resorption. The oils and fats obtained
under the process show an increase in effect of
the therapeutical remedies dispersed, dissolved or
emulsified in them which increase seems to be due
to an improved resorption, or to an influence ex-

exercised upon the admixed therapeutical agents by the accessory substances, which further continues to be incorporated in the oils or fats. If biologicco-therapeutically efficient crude oils are treated under this process, the finished products are not only readily assimilated by the human body, but also prove to possess a practically unaltered biological effect.

Biologicco-therapeutically efficient accessory substances of raw fats and oils are, for instance, the accessory substances contained in germ oils, in particular the vitamin-B-complex (α, β, γ -tocopherole, and the protective agents), vitamin A and vitamin D in their active condition, and in particular vitamin F of the liver oils. The new process implies the advantage that no special refining substances are to be used, and moreover this process shows the surprising effect that those biologically and therapeutically efficient accessory substances, which are thermolabile, are not detrimentally affected to any considerable degree. Furthermore due to the effect of the heat just those parts of the accessory substances contained in the raw fats and oils are precipitated, which would cause troubles in case of injection.

If particularly thermolabile accessory substances displaying biologicco-therapeutical effects, are present in the fats and oils, as, for instance, in the case of oestrogenous substances, it is advisable to carry out the heating action not only in the presence of an indifferent gas, but preferably in vacuo, or at a pressure above atmospheric, with an addition of small quantities of water or steam. In this manner it will be possible to refine the fats and oils at considerably lower temperatures. In this regard water and steam act as heat equalizing factors, as indifferent protective substances and as dishydrogenising agents.

In the refinement of raw fats and oils possessing a biologicco-therapeutical effect of their own, it ought to have been expected that the method of heating them would perfectly fail. At any rate, however, it could not be expected that the thermolabile accessory substances, which display a biologicco-therapeutical effect, would not suffer any important loss in efficiency by the treatment with heat within the meaning of the new process.

Finally, it is to be considered that the stability, and in consequence thereof the storing capacity of the fats and oils is improved by the process under the present invention, both from the biological point of view and under the aspects of chemistry of fatty substances. It is a well known fact that the processes obtaining in oils and fats which grow rancid, are of an extremely intricate nature, and that with regard to these processes according to recent considerations a particularly great importance is to be attributed to the fatty peroxides, which are formed. If stored fats and oils are exposed to the air, and that they bring about a so-called secondary oxydation of the neutral fatty matter within the meaning of a formation of fat aldehydes. If the fats and oils are treated under the new process, a reduction, for instance, of the vitamin E effect by the fatty peroxides is thereby prevented.

The process even permits to purify in such a way fats and oils, e. g. the highly unsaturated fats and oils of the types of wood oil, or of oiticica oil, which up till now were considered to be toxicant and therefore unserviceable for purposes of injection, that new therapeutical effects are imparted to them, which were hitherto unknown.

The finished products obtained under the new process cannot only be used separated for purposes of dispression, dissolution and emulsification, but also in combination with other efficient substances, and, if desirable, together with other neutral bodies.

As the raw fats and oils possessing a biologicco-therapeutical effect of their own, or not, frequently contain a great quantity of fatty acids in the free state, which exercise a disagreeable effect of irritation upon the skin at the place of injection, the primary substances and final products of the process can be esterified under the already known methods with glycerines or other multiple alcohols, e. g. sorbite, mannite, xylitane, or with other compounds with hydroxyl groups capable of esterification, whereby perfectly neutral final products are formed which can be injected and are readily assimilated.

The particularly important separation of the mucilaginous deposit from the treated fats and oils by filtration, in order to arrive at perfectly clear filtrates which later on will not separate any sediment, cannot be satisfactorily brought about by means of the hitherto known filtration methods and filtering devices, e. g. filter presses, suction filters with straining cloth, filter installations with vacuum cells. Therefore fats and oils, though refined under the new process, but purified in accordance with the hitherto known filtering methods, will not any longer, after having been stored for a prolonged period, during which they were exposed to varying external factors, e. g. variations in temperature, come up to the high demands made with regard to their purity and sedimentation upon fats and oils, which can be injected and are readily assimilated. This is not probably due to the fact that small traces of humidity still remaining in the finished product will probably bring about a precipitation of the phosphatides and sterines still existing in the fats and oils which have been treated, in particular in cases where water or vapor have been used, which precipitation will be particularly troublesome in the ampullae filled with the final product.

As a further development of this invention, it has now been found that these difficulties can be obviated by the use of a hygroscopic filtering matter possessing an active surface, e. g. dried sawdust. For this purpose sawdust of pine wood, fir wood, or larch wood, or mixture of same, are particularly well suitable. The filtration of fats and oils by means of sawdust, which is already known in itself, has most probably not yet been used for the preparation of injectable and readily assimilated fats and oils with, or without, biologicco-therapeutical effects of their own, because it had been assumed that the finished article would be made impure by particles of sawdust or wood powder, or that resinous substances and wood meal would enter the preparation to be used for purposes of injection. It was, however, found that not only this danger does not actually exist, but that, on the contrary by the use of sawdust a novel filtering effect is brought about, which exercises an advantageous influence upon the final product, which can be used for injection and is readily assimilated.

In order to filter the oils and fats, it is preferable to use two or more filters which are arranged one above the other in such a way that the process of filtration in one of the filters is performed in downward direction, whereas the passage through the lower one, with the aid of the hydro-

static pressure of the roughly filtered fats and oils takes place from bottom to top, i. e. with the use of counter-flow, wherefore small particles of sawdust or other dust after a preliminary period of operation of the filtering plant cannot be further carried along together with the filtrate, and moreover an intimate contact between the sawdust and the material to be filtered is rendered possible for purposes of dehydration, for drying, adsorption and absorption of the easily dischargeable ballast substances. The velocity of flow can be controlled by means of a cock inserted between the first and the second filtering vessels, and by the admission cock of the store tank. As a matter of course the number, order, and arrangement of the pre-filtering and re-filtering devices can be varied at direction, though it has also been found to be preferable that the re-filtering device with its direction of flow from bottom to top is placed at the end of the series of filters.

It is, however, also possible to prepare fats and oils with or without a biologic-therapeutical effect of their own, which are highly serviceable, can be injected and are readily assimilated by the body, if the asbestos filters customary for "clarifying" are used, which have a sterilizing effect. i. e. are able to retain microbes, or still better, so-called F-K filters, e. g. those manufactured by the Seitz-Werke at Kreuznach, Germany, are used, or if the material used for the reaction, is not filtered, but freed of both the deposit and water in a purifying centrifuge, i. e. an Ultra-centrifuge or a high-efficiency centrifuge.

Examples

(1.) 100 kg of raw, cold-pressed wheat germ oil, which by its nature contains oestrogenous substances of the type of the follicle hormone, and shows vitamin-E contents corresponding to a biological effect of 50 Pacini-Linn units per g and a Lea figure of 50, are in a glass-enameled conical vessel, which under any circumstances must be free of iron and copper, heated to 110 centigrades for about 10 minutes upon permanent strong agitation with an admixture of 1% of water, and upon blowing through nitrogen gas. An indifferent gas is blown through further upon slow cooling, whereafter a settling period of about 2 to 3 days follows: In the course of this time in the treated oil a flaky sediment is deposited, which together with a portion of the water previously admixed is collected at the bottom of the vessel. The oil is separated from the sediment in such a way that the oil is tapped with a siphon and passed through filtering layers of dried sawdust, as described above. The finished product thus prepared is perfectly clear, and will also continue to be free of substances resulting in turbidity, even if stored for a prolonged period at varying temperatures. Its vitamin-E contents have been left unaltered, as compared with those ascertained in the case of the primary material, the Lea figure was considerably reduced by the treatment, and now only amounts to 3 units.

The clear wheat germ oil can be directly filled into ampullae. In tests with animals it will continue to show the originally existing effect causing oestrus, which most probably is due to the oestrogenous substances.

(2.) 100 kg of raw wood oil are upon careful stirring quickly heated in an aluminium vessel up to 160 centigrades upon blowing through nitrogen gas, whereupon it is cooled down just as quickly to about 0° by means of an intense tubular cooling device operated with cooling brine. Thereby a fine, flaky deposit is formed, which mainly consists of mucilage, in particular albuminous substances. A sterile oil suitable for injection and capable of ready assimilation is obtained, if the separated final product is filtered through a so-called "Seitz" filter with F-K filtering substances suitable for purposes of sterilization. By intramuscular injection of the highly unsaturated, purified wood oil quite novel therapeutical effects can be brought about, among others an intense influence upon the metabolism of fatty substances and hydrocarbons in the living.

(3.) 100 kg of raw gingili oil (sesame-oil) having an acidity figure of 0.63 are, upon blowing through carbonic acid gas, heated for two hours up to 220°, and 130 g of glycerine are upon stirring gradually admixed thereto for the purpose of esterification. Thereupon the mixture is quickly cooled down to zero, as described in example 2, and filtered through a filtering device filled with sawdust. The clear gingili oil thus obtained has an acidity figure of 0, and is particularly well adapted to dispersion or dissolution of any therapeutical remedies whatsoever.

(3.) 100 kg of raw halibut liver-oil with vitamin-A contents of 2500 I. U. per g, and vitamin-D contents of 1500 I. U. per g are heated for 1 to 3 minutes in a current of carbon dioxide up to 160 centigrades in an instantaneous heating device, e. g. of the "Tödt" type, as it is used for the pasteurization of milk (cf. Ullmann, "Enzyklopädie der technischen Chemie," Vol. 4, 2nd edition, p. 557 of 1931) and then, after having been cooled to 5 centigrades below zero point by a highest efficiency centrifuge of the "Padberg" type. The resulting substance is suitable for injection, and is to a high degree freed of "liver-oil stearin" with not much altered vitamin-A and vitamin-B contents, which oil will not be turbidified later on.

It is intended to make such oils suitable for purposes of injection under the new process, as are of acid character by their nature and contain vitamin susceptible to be impaired by heat and atmospheric oxygen, it is possible to treat these oils with aqueous monovalent alcohols in order to remove the free fatty acids, as practically only the free fatty acids are dissolved by the aqueous alcohol and thus eliminated from the oil, whereas the biologically efficient agents are almost insoluble in it.

FELIX GRANDEL.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF HALOGENATED 1-HYDROXY-5,6,7,8-TETRAHYDRONAPHTHALENES

Winfried Hentrich, Rodleben B. Dessau-Rosslau,
and Wilhelm Kaiser, Dessau, Germany; vested
in the Alien Property Custodian

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This invention relates to halogenated 1-hydroxy-5,6,7,8-tetrahydronaphthalenes and to a process for their manufacture. The object of this invention is to provide a simple and feasible method for producing disinfectants and preservatives.

It has been found that excellent disinfectants and preservatives, which are as to their efficiency most superior to the usual phenols, can be obtained by treating 1-hydroxy-5,6,7,8-tetrahydronaphthalene or its 2-alkyl or 2-halogen substitution products with halogenating agents. In this case a halogen atom takes the 4-position of the initial material.

Hydroxy-tetrahydronaphthalenes, which may be used for the process are in first line e.g. 1-hydroxy-5,6,7,8-tetrahydronaphthalene, 1-hydroxy-2-methyl-5,6,7,8-tetrahydronaphthalene and 1-hydroxy-2-chloro-5,6,7,8-tetrahydronaphthalene as well as those substitution products of these compounds, which in 4-position contain groups replaceable by halogen such as sulfo, carboxyl, nitro or acylamino groups. As halogenating agents all those agents are suitable which usually are applied for the halogenation of phenols e.g.: chlorine, bromine either liquid or in vapour form, iodine, mixtures of permanganate and hydrohalic acid, sulfuryl chloride, phosphorous oxychloride and the like. Into the non-substituted 1-hydroxy-5,6,7,8-tetrahydronaphthalene one or several halogen atoms may be introduced according to the applied amount of halogenating agents. In applying sulfuryl chloride chiefly the halogenation in 4-position to the hydroxyl group is performed, so that the 4-chloro-1-hydroxy-5,6,7,8-tetrahydronaphthalene is obtained, which may be converted by further halogenating into a 4-chloro-2-halogen-1-hydroxy-5,6,7,8-tetrahydronaphthalene.

Example

660 parts by weight of 1-hydroxy-5,6,7,8-tetrahydronaphthalene (fusing point 65 to 67° C.) are dissolved in 1600 parts by weight of carbon tetrachloride and mixed within 3 hours with 660 parts by weight of sulfuryl chloride at 30 to 40° C. Then the temperature is gradually raised and the reaction mass is finally heated at the reflux-

cooler for 2 hours up to boiling. Now by distilling off the auxiliary stuffs are separated and the reaction product is distilled over at 175 to 180° C under a Hg-pressure of 23 mm. It solidifies while cooling down to a colourless crystalline mass fusing after the recrystallising from benzine at 68 to 69° C. The yield of 1-hydroxy-4-chloro-5,6,7,8-tetrahydronaphthalene will be about 75% of the theory. Little amounts of 1-hydroxy-2-chloro-5,6,7,8-tetrahydronaphthalene may be obtained from the mother liquor of the benzine and may be converted by afterchlorinating into the 1-hydroxy-2,4-dichloro-5, 6, 7, 8-tetrahydronaphthalene which will be obtained likewise by acting more considerable amounts of sulfuryl chloride upon the 1-hydroxy-compound. The treatment of the 2-chloro-1-hydroxy-compound with bromine leads to the 1-hydroxy-2-chloro-4-bromo-5,6,7,8-tetrahydronaphthalene.

The aforesaid compounds are soluble in diluted alkali lyes, aqueous solutions of soaps and soap substitutes such as fatty alcohol sulfonates, organic solvents such as alcohol and the like. They may be applied either alone or mixed with other disinfecting media and eventually with an addition of diluents or stretching agents for the disinfection of commodities, medical instruments, textiles, linen, walls, tiles, floors, implements, apparatus used in the alimentary and appetizing products industry, as well as for the disinfecting of animals and parts of the human body. Moreover they are apt for the preserving of perishable animal and vegetable goods such as pastes and sizes, furs, hides, skins and the like.

(a) A 0.02% solution of 1-hydroxy-4-chloro-5,6,7,8-tetrahydronaphthalene kills at 15° a deposit of bact. coli commun or of bact. staphylococcus aureus completely within 2.5 minutes.

(b) 0.01% 1-hydroxy-4-chloro-5,6,7,8-tetrahydronaphthalene added to a sugar solution preserves this solution against fermentation and mold.

(c) 0.01% 1-hydroxy-4-chloro-5,6,7,8-tetrahydronaphthalene are added to a steeping liquor for hides. The liquor and the hides steeped therein are preserved against decomposition.

WINFRID HENTRICH.
WILHELM KAISER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PRODUCING VINYL CHLORIDE

Erich Schaeffer, Burghausen, Germany; vested in the Alien Property Custodian

No Drawing. Application filed October 12, 1940

This invention relates to the production of vinyl chloride and has for its object to provide a new and improved process for this purpose.

It is known to pass a mixture of acetylene and hydrochloric acid gas over mercury compounds, for instance mercury chloride, at elevated temperatures, for the purpose of producing vinyl chloride in the vapor phase. During the conversion the mercury compounds are reduced to mercury, which sublimates out of the reaction chamber, so that the catalyst has only a very short life. With other known catalysts, for example compounds of zinc, aluminum, iron and of metals of the second and fifth groups of the periodic system, the conversions are considerably less, and considerably higher reaction temperatures are required in order to start the conversion at all. The effect of these catalysts deteriorates too quickly for technical purposes and they also promote the formation of by-products, for instance ethylidene bichloride.

I have found that of the last-mentioned known catalysts, the chlorides of alkaline earth metals, and mixtures thereof, particularly chloride of strontium, chloride of barium, chloride of calcium, have imparted to them a considerably increased effectiveness and longer life when there is incorporated in them small quantities of mercury compounds, for instance mercury chloride. In comparison with other metallic chlorides, these novel catalysts lead substantially only to the formation of vinyl chloride, while undesirable by-products, such as ethylidene bichloride, do not generate to any appreciable extent. It is surprising that the mercury compounds remain in the catalyst, so that the favorable conversion conditions are maintained for a long period, as much as 1000 hours and more. In general a content of 0.1-2% mercury salt is sufficient in the catalyst. Reaction temperatures of over 120° C. are preferable, which may be increased during the reaction to something like 250° C. in case the conversion drops.

The introduced gas mixture may consist of 1 mol of acetylene and 1 mol of hydrochloric acid gas. However, acetylene can also be advantageously used in excess up to about four-fold, the excess acetylene being returned to the reaction zone upon the separation of the vinyl chloride. Super-atmospheric pressure may be used in the

conversion. The catalyst is used either alone or preferably when charged upon porous carriers, particularly those with high surface activity, such as activated charcoal, silica gel, and the like. In the production of the catalyst the procedure followed is that, for example, 0.1-0.2% mercury chloride is mixed with a hot aqueous solution saturated for instance with barium chloride. The water is then removed by evaporation. The solution can also be mixed with other substances known as catalysts. When porous carriers are used, these are saturated with the solution and the water is then removed.

Example 1

Highly activated charcoal or silica gel is soaked with a hot saturated solution of barium chloride, which contains 0.2% mercury chloride, and is then dried. At a temperature of 160-250° C., a gaseous mixture of 200 litres of acetylene and 120 litres of hydrochloric acid gas is passed per hour through a reaction chamber of a volume of 6 litres filled with the catalyst. 300-330 g. vinyl chloride is obtained per hour, which is separated in the conventional manner from the acetylene by washing with solvents or by absorption with activated charcoal or by cooling. Only after 500 hours does the conversion drop by about 30%. Without a content of mercury chloride in the catalyst a higher temperature is necessary and after only 200 hours the conversion is reduced to less than one-half of the above-indicated quantities of vinyl chloride.

Example 2

Activated charcoal is saturated with a solution which contains about 20% calcium chloride, 10% barium chloride and 1% mercury chloride. A gaseous mixture of 6 cubic meters of acetylene and 3-4 cubic meters of hydrochloric acid gas is passed per hour through a reaction chamber of a volume of 160 litres filled with the catalyst, at a temperature of 120° C. In this case 8-9 kilos of vinyl chloride are produced per hour, the vinyl chloride being separated in the usual manner from the excess acetylene, and the acetylene is returned into the reaction chamber. If the catalyst contains no mercury salt, no reaction takes place at 120° C. at all.

ERICH SCHAEFFER.

ALIEN PROPERTY CUSTODIAN

PROCESS OF HEAT-TREATING POLYMERIZATION PRODUCTS

Carl Zerbe, Hamburg 36, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed October 14, 1940

This invention relates to heat-treating polymerization products of butadiene and its homologues and mixed polymerization products thereof.

According to a known process, the workability of polymerization products of butadiene, its homologues and mixed polymerization products thereof with styrene and acrylonitrile is improved by heating to temperatures of 120° to 170° C and simultaneous partial oxidation by the air present or other oxygen yielding agents. It is exclusively due to this so-called thermal decomposition that some products of this class can be practically utilized.

It has been found now that this process can be improved by carrying out the heat treatment of the polymerization products or mixed polymerization products in the presence of organic difficultly volatile substances having a swelling effect thereon, as the preferably polycyclic hydrocarbons or hydrocarbon mixtures obtained in the refining of mineral oils and wholly or partly soluble in concentrated sulfuric acid. The process may be applied in the presence of air or of air enriched by oxygen or in an atmosphere of indifferent gas. Compared with the known addition of these substances to the polymerization products mentioned after thermal decomposition, the process affords the advantage of more intense swelling and better distribution of the usually tight particles of these products.

Particularly suitable in this respect are for example the hydrocarbon mixtures obtainable from the residue accruing in refining mineral oils with concentrated sulfuric acid or selective solvents. Owing to their partly unsaturated character, these hydrocarbons are largely soluble in concentrated sulfuric acid and are separated from the crude mineral oils either by sulfuric acid or so-called selective solvents, as sulfur dioxide, benzene mixtures, furfurole, etc., which can be extracted from the residue mentioned by neutralization and/or distilling. If selective solvents are employed the hydrocarbons may be applied directly after the removal of the solvents.

In the same way other high-boiling unsaturated and/or polycyclic hydrocarbon mixtures can be used according to the invention, and also products containing them in larger quantities and occurring either in nature like miri oil of Borneo,

rich in substances showing a tendency to resinify, or obtainable by synthesis.

Additions of the class mentioned to the polymerization products or mixed polymerization products during thermal decomposition insure not only good workability but also preserve these products to a considerable extent due to the fact that access of atmospheric oxygen is rendered more difficult. The quality of the vulcanizates made from products according to the invention is not only maintained by the additions but partly appreciably improved thereby.

As hydrocarbon mixtures of the kind specified have proved excellent aids, usable also in relatively large quantities, to natural and synthetic rubber and rubber like substances, their employment according to the invention is often particularly desirable.

Another important feature is that the temperature and also the duration of the heat treatment can be reduced in thermal decomposition while using the substances mentioned. As under existing conditions the decomposition temperature must be in the neighborhood of, say, 140° C to have good effects, it will be understood how valuable an agent is through which these conditions which are quite severe for the unstable mixed polymerization products may be modified.

Dispersion of the hydrocarbons or hydrocarbon mixtures to be added in a manner most favorable to the performance of the process can be attained by carefully mixing crumbs or bits of the polymerization or mixed polymerization products with the hydrocarbon mixture, made thinly liquid by slight heating, in a suitable apparatus. It is further possible to bring about a particularly fine dispersion of the hydrocarbon mixture in the products mentioned by adding to emulsions of the latter the hydrocarbon mixtures according to the invention in emulsified form or emulsifying them therein and then coagulating this mixture, whereupon the coagulum formed is freed by washing from most of the dispersing or emulsifying agents and subjected to the usual subsequent treatment.

The following example has been found to give good results:

Example

A mixed polymerization product of butadiene and styrene, known under the trade name

"Buna-S," was mixed in a suitable apparatus with 15% of a product obtained by neutralizing an acid tar obtained by refining heavy mineral oils with concentrated H_2SO_4 and subsequent distillation. The mixture was heated to 135° to 140° C for one to two hours in the presence of air, then homogenized on a roller and used for preparing a mixture having the following composition:

	Parts	10
Treated substance -----	1,150	
Soot, active -----	470	
Zinc oxide -----	47	
Sulfur -----	1.8	
Stearic acid -----	1.8	15
Vulcazit AZ -----	1.2	

In a parallel experiment the synthetic rubber alone was subjected to thermal treatment and the adjuvant substance mentioned, in accordance with the usual practice, admixed only after the thermal treatment of the synthetic rubber to-

gether with the other additions. The preparation of a homogeneous mixture was in this instance more difficult and consumed more time.

During the connecting heating in stages of 5 20, 30 and 40 minutes at 133° C the following data could be observed:

	Resistance to fracture	Breaking elongation or stretch
	<i>Kg./cm.²</i>	<i>Per cent</i>
Normally decomposed substance -----	20' 135 30' 183 40' 175	551 520 426
Substance treated accdg. to invention -----	20' 168 30' 207 40' 186	571 558 485

These data clearly show that the process according to the invention yields vulcanizates of higher value.

CARL ZERBE.

ALIEN PROPERTY CUSTODIAN

CORROSION PREVENTING AGENTS

Franz Giloy, Dessau, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed October 17, 1940

This invention relates to corrosion preventing agents and particularly to protecting metals against corrosion by water. A further object of the invention is to protect metals against corrosion by water containing fluids and solutions.

It has been found that the corrosion of metals and metallic articles particularly of those made of iron, iron alloys or steel occurring in the presence of water, water containing fluids and solutions with a pH value lying not below 6.5 is prevented by adding to said liquids the water soluble salts of ether carboxylic acids of the general formula $(R.O.)_x.R'.COOH$. In this general formula R stands for any organic radical containing at least 4 carbon atoms which may also be cyclically arranged and which may be interrupted by hetero atoms or hetero atom groups, whereas R' means an alkylene radical which may also be substituted and x the numbers 1 or 2.

Ether carboxylic acids of this kind are e. g. butyloxy acetic acid, i-amylloxy acetic acid, mixtures of alkoxy acetic acids obtainable from mixtures of alcohols obtained by reduction of first running acids of the paraffin oxidation or obtained as high boiling portions at the methanol synthesis, octyloxy acetic acid, dodecyloxy acetic acid, cyclohexyloxy acetic acid, tetrahydrofurfuryloxy acetic acid, phenoxy acetic acid, cresoxy acetic acid, arylloxy fatty acids alkylated or cycloalkylated in the nucleus, naphthenyloxy acetic acids, abietyloxy acetic acids, benzyloxy acetic acid, tetrahydromenaphthyloxy acetic acid, dioctyloxy acetic acid, α -heptyloxy propionic acid, β -octyloxy propionic acid, γ -octyloxy-iso-butyric acid, α -octyloxy capric acid and the like. Furthermore alkoxy fatty acids may be used, which are obtained from secondary alcohols by converting with halogen fatty acids, the alcohols being obtained from the first running acids of the paraffin oxidation with 7 to 9 carbon atoms by ketonizing and subsequent hydrogenizing or such alkoxy fatty acids, which are obtained by reacting alcoholates of the primary alcohols C_7-C_9 with α -halogen fatty acids such as α -butoxy lauric acid, 6-hydroxy-n-hexyloxy acetic acid, methoxyn-hexyloxy acetic acid and the like. Among these ether carboxylic acids the alkoxy and cycloalkoxy fatty acids are to be preferred.

In aqueous solution the salts of those acids which may be formed with alkali, earth alkali and earth methals, ammonia or organic bases, prevent the corrosion of metals particularly of iron, iron alloys and steel and of articles made thereof. The concentration of the salts of the ether carboxylic acids in the water may vary within wide limits, it amounts to 0.01-5 percent and more related to the water.

The anticorrosive effect is obtained not only in water but also in water containing fluids and solutions having a pH value of 6.5 or more.

Therefore the water may have addition agents which have a neutral, weak acid or alkaline character and which may act in a certain extent corroding such as acetone, methanol, ethanol, butanol, glycerine and the like, as well as aqueous metal salt solutions such as solutions of ammonium chloride, calcium chloride of acetate of alumina.

Furthermore the water may contain known disinfecting means such as dimethylamino-acetic acid-dodecylamide-chloro-benzylate, piperidine-acetic acid-dodecylester-chloro-benzylate, dimethyl-dodecyl-benzyl-ammonium-chloride, dimethyl-dodecyl-amino-acetate, 4-isooctylphenoldimethyl-amino-ethyl-ether-chloro-benzylate.

The afore described corrosion preventing agents may also be applied in combination with other known and equally efficient agents such as chromates, nitrites or triazotates.

The corrosion preventing agents are used for water or any water containing fluids or solutions which are in contact with metals particularly iron or iron articles such as water containing fluids and fluid mixtures for technical apparatuses as gas meters, aqueous systems of heating and refrigerating apparatuses, aqueous systems of internal combustion engines, aqueous systems of break and pressure devices, for shock absorbers, driving gears and the like. Furthermore the anti-corrosive agents can be added to water containing fluids for cleaning and preserving razor apparatuses, razor blades and medical instruments. Finally the agents may be used for preparations for working metals such as aqueous oil emulsions for boring or cutting metals, lubricating emulsions and the like.

Example 1

In an 1% aqueous solution of piperidino-acetic acid-dodecyl-ester-chlorobenzylate containing moreover 3 to 4% of the ammonium salts of a mixture of alkoxy acetic acids the alkyl groups of which have 7 to 9 carbon atoms, any metallic articles e. g. razor blades, remain absolutely stainless even after a several days' standing. At the contrary, without the addition of said ammonium salt the forming of rust spots will be observed already within a few hours.

Example 2

67 parts by weight of a mineral oil are mixed while stirring with 33 parts by weight of the ammonium salt of the butoxy acetic acid, whereupon 4 parts by weight of ammonia (25%) are gradually added. The mixture is stirred until a clear suspension is obtained. 2 parts by weight of this mixture are stirred in 100 parts of water forming a rust preventing emulsion which may be used as lubricating and boring oil.

FRANZ GILOY.

ALIEN PROPERTY CUSTODIAN

POLYMERIZATION OF BUTADIENES

Kurt Meisenburg and Ingofroh Dennstedt, Leverkusen I. G.-Werk, and Ewald Zaucker, Halle an der Saale, Germany; vested in the Alien Property Custodian

No Drawing. Application filed October 17, 1940

The present invention relates to a new process of polymerizing butadienes-1.3 and to the new polymerizates which are obtainable thereby.

It is known that the polymerization of butadienes-1.3 easily results in the formation of products which are insoluble in benzene and resemble vulcanized rubber rather than the unvulcanized product. In consequence thereof, the working of these products on the roller and the incorporation therewith of filling materials and the ingredients which are necessary for effecting vulcanization is connected with considerable difficulties. Moreover, the mechanical properties of the vulcanizates obtained from such products are materially impaired when compared with those vulcanizates obtained from benzene soluble polymerizates. In order to avoid these disadvantages it has been proposed to effect the heat polymerization of butadienes-1.3 in the presence of sulfur or certain sulfur containing compounds. It is not disputed that certain improvements are obtained thereby; however, by the use of these additions the disadvantage is involved that the course of the polymerization is considerably retarded; moreover, the presence of sulfur and the said sulfur containing compounds may result in the formation of undesired dimeric by-products.

It is the object of the present invention to do away with these disadvantages and to develop a new process which allows one to polymerize butadienes-1.3 in a nearly quantitative yield without retarding the course of the reaction and without involving the formation of products which are insoluble in benzene or of dimeric products. Other objects of our invention will be apparent from the following description and claims.

It has been found that organic sulfur containing compounds which are soluble in the monomeric products to be polymerized exert a remarkable regulating effect upon the course of the emulsion polymerization. Those sulfur containing products are preferred which contain at least 2 sulfur atoms directly connected with each other, i. e. organic disulfides. Examples for suitable regulators are dialkylxanthogendisulfides and di(benzoic acid ester)tetra sulfides. In most cases an amount of less than 1% of these regulators (calculated on the amount of monomeric products) is sufficient to exert the desired effect; in other cases somewhat higher amounts are required. Depending on the amount of the regulators the resulting polymerizates either resemble natural rubber or are of a more plastic nature, the yield and solubility in organic solvents such as benzene being excellent regardless of the amount of such regulators. In this respect our

new process is superior to the hitherto employed heat polymerization in the presence of sulfur and sulfur containing compounds, since in the latter case the amount of the regulators must be carefully controlled if a good yield is to be combined with a good solubility of the polymerizates.

The new process can be applied to every polymerizable butadiene-1.3, the latter term being intended to comprise the unsubstituted butadiene as well as the homologues and substitution products thereof such as isoprene, 2-chlorobutadiene-1.3 or 2-bromo-butadiene-1.3. As a matter of fact, also mixtures of such butadienes with other polymerizable compounds such as styrene or acrylic acid nitrile can be employed. It is to be understood that such sulfur containing regulators are preferred, as have only a weak vulcanizing effect or no such effect at all.

The following examples illustrate the present invention without, however, restricting it thereto the parts being by weight:—

Example 1

0.5 part of diisopropylxanthogendisulfide dissolved in 69 parts of butadiene are emulsified in 200 parts of a 5% sodium oleate solution containing 0.3 part of ammonium persulfate. After a several days' shaking a soluble plastic polymerizate is obtained in a quantitative yield.

Example 2

0.1 part of diisopropylxanthogendisulfide dissolved in 52 parts of butadiene and 22 parts of styrene are emulsified in 200 parts of a 5% sodium oleate solution containing 0.3 part of ammonium persulfate. After a several days' shaking at 30° and upon coagulation there is obtained in a nearly quantitative yield an easily soluble mixed polymerizate which shows excellent mechanical properties.

Example 3

0.2 part of diisopropylxanthogendisulfide dissolved in 47.5 parts of 2-chlorobutadiene-1.3 and 50 2.5 parts of 1-phenoxypropeneoxide-2.3 are poured into 50 parts of a 2% sodium oleate solution while thoroughly stirring and kept at a temperature of 20–30°. In a nearly quantitative yield a benzene soluble polymerizate is thus obtained.

Example 4

0.4 part of diethylxanthogendisulfide dissolved in
 180 parts of 2-chlorobutadiene-1.3,
 10 parts of acrylic acid nitrile and
 10 parts of 1-phenoxypropeneoxide-2.3 are poured into
 200 parts of a 2% sodium oleate solution.
 On working up a soluble polymerizate is obtained which can easily be rolled and which on vulcanizing shows excellent mechanical properties.

Example 5

0.1 part of di-(benzoic acid methylester)-tetrasulfide are dissolved in
 47.5 parts of 2-chlorobutadiene-1.3 and
 2.5 parts of 1-phenoxypropeneoxide-2.3.
 Thereupon this solution is emulsified in 50 parts of a 2% sodium oleate solution. In a good yield a soluble polymerizate is thus obtained which can easily be worked up.

Example 6

0.4 part of diisopropylxanthogendisulfide are dissolved in
 180 parts of 2-chlorobutadiene-1.3,
 10 parts of styrene and
 10 parts of phenoxypropeneoxide;
 thereupon this solution is emulsified in 200 parts of a 2% solution of di-isobutyl naphthalene sulfonate containing 8 parts of sodium lye. On polymerizing at 20-30° a soluble product is obtained which can easily be worked up on the roller and which on vulcanizing shows excellent mechanical properties.

Example 7

75 parts of butadiene and
 25 parts of styrene are emulsified in
 142 parts of water having dissolved therein
 5 3 parts of sodium diisobutyl naphthalene sulfonate
 0.2 part of sodium hydroxide and
 0.375 part of potassium persulfate.
 Polymerization is effected by a 5 to 6 hours' shaking at 30°. The following table shows the yield of soluble polymerizates obtained under the influence of varying amounts of tolyldi-sulfide as regulator:

	Amount of regulator in per cent of polymerizable substances	Yield of soluble polymerizates in per cent of the theoretical amount
15		
20	3	91
	4	92
	5	92

Example 8

100 parts of 2-chlorobutadiene-1.3 are emulsified in
 100 parts of a 2% sodium oleate solution and with the addition of
 3 parts of 1-phenoxypropeneoxide-2.3.
 Polymerization is effected by a 4 to 5 hours' heating to 30°. The yield of soluble polymerizates is 78% even if only 1% of tolyltrisulfide is present as regulator.

KURT MEISENBURG.
 INGOFROH DENNSTEDT.
 EWALD ZAUCKER.

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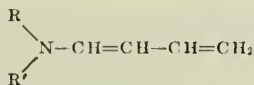
PROCESS FOR PRODUCING CONDENSATION PRODUCTS

Christoph Grundmann, Dessau, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed October 17, 1940

The invention relates to a process for producing higher molecular polyenealdehydes from acetaldehyde.

It is known that crotonaldehyde and its vinylene homologues as hexadienal, octatrienal, decatetraenal, dodecapentaenal may be condensed in the presence of secondary organic bases or their salts with organic acids respectively to straight chained polyenealdehydes (polyenals). However according to the literature these condensation products are obtained in a comparatively small and varying yield. As chief products of the reaction cyclic bodies are formed. The explanation of the mechanism of this condensation has shown, that the intermediate product of this reaction is 1-dialkylaminobutadiene of the formula



which as diene is easily added to dienophile compounds while forming derivatives of the dihydrobenzol. Under the conditions of the condensation hitherto applied i. e. by working with non-diluted crotonaldehyde in the presence of little amounts of a catalyst this reaction is greatly promoted, as it is most probable that the reactive intermediate product is caught by the dienophile components e. g. crotonaldehyde present in a considerable excess.

Now it has been found that higher linear polyenals and especially polyenals with no less than 12 carbon atoms are obtained in a very satisfactory yield when proceeding at the condensation from the acetaldehyde and when keeping the reaction temperature advantageously near to the boiling point of the acetaldehyde. So in the midst of the acetaldehyde the developing intermediate products will have a reduced possibility of entering into dienesyntheses and therefore the linear condensation will be preferred. The polyenals may be converted in a usual way

into carboxylic acids of an equal or higher molecular weight, into aldehydes with a higher percentage of hydrogen as well as into the corresponding primary alcohols, which may serve for well known technical purposes. The thus obtained mixtures represent either as such or in the form of their fractions, a valuable substitute for fatty acids, fatty aldehydes and fatty alcohols.

Example

156 parts by weight of acetaldehyde (98 to 100%) are mixed with 4 parts by weight of piperidine and with acetic acid of the amount required for neutralisation and kept by cooling at 15 to 20°C. After the heat effect is disappeared the equal amount of the catalyst is added and this operation is repeated once more while increasing the temperature to 25°C. After a 16 hours' standing at 15 to 20°C a thick dark-red mass of a mixture of crystallised polyenals is obtained which is purified by washing with methanol. The obtained polyenals are very difficultly soluble in the usual solvents. They may be converted by hydrogenation in a known manner into saturated aldehydes or saturated alcohols respectively.

Instead of the piperidine acetate as catalysts other salts of secondary organic bases may be used such as piperidine formate, piperidine butyrate, piperidine crotonate, piperidine chloroacetate, piperazine mono- or diacetate, morpholine acetate, diethylamine acetate, dibutylamine acetate and the like. The amount of the catalysts may vary between 1-10 percent related to the acetaldehyde. The reaction temperatures in general are below 100° preferably near the boiling point of the acetaldehyde of 21°. Furthermore the condensation process may be carried out under pressure or in the presence of organic solvents as diethylether, dibutylether, dioxane and the like.

CHRISTOPH GRUNDMANN.

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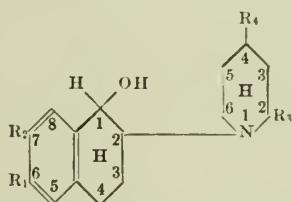
ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF ANALGETICALLY ACTIVE TETRAHYDRONAPHTHOLS

Georg Scheuing and Bruno Walach, Ingelheim A. Rh., Germany; vested in the Alien Property Custodian

No Drawing. Application filed October 19, 1940

It has been found that the 1-oxy-2-piperidyl-1,2,3,4-tetrahydronaphthalenes of the general formula:



possess a strong analgetic action at a comparatively small toxicity.

In the foregoing general formula R_1 and R_2 mean hydrogen atoms, oxy, alkyloxy or alkyl groups and R_3 and R_4 hydrogen atoms or alkyl groups.

The production of the compounds according to the invention is carried out by known methods, in that the corresponding 1-oxo compounds are reduced for instance by catalytic hydrogenation or reduction by aluminum amalgam etc. The 1-oxo compounds used as the starting material can be obtained for instance by the process according to the U. S. A. Patent (Application Serial Number 309,702) by reacting the 1-oxo-2-halogenetetrahydronaphthalenes with piperidines in the presence of organic solvents with the exception of anhydrous methyl alcohol.

As especially good analgetics were found the 6-methoxy-1-oxy-2-N-piperidyl - 1,2,3,4-tetrahydronaphthalene with a m. p. of 110°C (m. p. of the hydrochloride 206°C) and the 6-methoxy-1-oxy-2-N(2,4-dimethylpiperidyl) - 1,2,3,4-tetrahydronaphthalene (m. p. of the hydrochloride 183°C) as well as the corresponding ethoxy and butoxy compounds.

Strauss has described (see Berichte der deutschen chemischen Gesellschaft vol. 54 (1921) p. 40 and following, especially p. p. 59 and 62) a compound, which he has formulated as the 1-oxy-2-piperidyl - 1,2,3,4-tetrahydronaphthalene. Von Braun supposes (see the same paper vol. 55 (1921) p. 3648 and following especially p. 3655) its constitution to be that of the 1-oxy-2-piperidyl - 1,2,3,4-tetrahydronaphthalene. But the known compound is the 1-piperidyl-2-oxy-tetrahydronaphthalene, this following from the fact that by the catalytic hydrogenation of the 1-oxo-2-piperidyltetrahydronaphthalene an oxy compound results, which is different from the known compound. However the constitution of the compound obtained by the catalytic hydrogenation of the 1-oxo-2-piperidyltetrahydronaphthalene

is verified by the process of its preparation, especially in accordance with researches concerning the production of the synthetic adrenaline and ephedrine.

In the following the process according to the invention may be explained on hand of some examples, no limitations as to the starting materials, the proportions of their quantities, the temperatures etc. stated in these examples, being intended.

EXAMPLE 1.—6-methoxy-1-oxy-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene

80 g of the hydrochloride of the 6-methoxy-1-oxy-2-piperidyl - 1,2,3,4-tetrahydronaphthalene with a m. p. of 203°C dissolved in 500 cc of methyl alcohol are hydrogenated with 30 g of a nickel catalyst under a hydrogen pressure of 200 atm at 110–120°C. The hydrogen addition stops as soon as about 1 mol of hydrogen is taken up. From the resulting solution one obtains 60 g of the base with a b.p. of 177°C at 0.3 mm Hg in a yield of 86% of the theory. When crystallised out of petrol it melts at 110°C. The hydrochloride has a m.p. of 206°C; beside this 6 g of an isomeric compound (m.p. of the hydrochloride 196°C) in a yield of 8.5% of the theory are to be obtained.

EXAMPLE 2.—1-oxy-2-N-piperidyl-1,2,3,4-tetrahydronaphthalene

25 g of the 1-oxo-2-piperidyl-1,2,3,4-tetrahydronaphthalenic base with a b.p. of 183°C at 0.3 mm Hg (m.p. of the hydrochloride 203°C) dissolved in 500 cc of methyl alcohol are hydrogenated with 30 g of a nickel catalyst at 100–120°C under a hydrogen pressure of 200 atm until the hydrogen absorption stops. 20 g of the base with a b.p. of 189°C at 0.1 mm Hg in a yield of 80% of the theory are obtained. The hydrochloride has a m.p. of 200°C (the mixed melting point (Mischschmelzpunkt) with a comparison material lays at 165–178°C).

EXAMPLE 3.—6-methoxy-1-oxy-2-N- α -pipecolyl-1,2,3,4-tetrahydronaphthalene

32.6 g of the hydrochloride of the 6-methoxy-1-oxo-2- α -pipecolyl-1,2,3,4-tetrahydronaphthalene with a m.p. of 192°C dissolved in 500 cc of alcohol are hydrogenated with 20 g of a nickel catalyst as above-mentioned. 20.6 g of the aminoalcohol with a b.p. of 172°C at 0.1 mm Hg in a yield of 72% of the theory are obtained. The hydrochloride has a m.p. of 198°C; the mixed

melting point (Mischschmelzpunkt) lays at 177°C.

EXAMPLE 4.—6-methoxy-1-oxy-2-N(2,4-dimethylpiperidyl)-1,2,3,4-tetrahydronaphthalene

25 g of the hydrochloride of the 6-methoxy-1-oxo-2(2,4-dimethylpiperidyl)-1,2,3,4-tetrahydronaphthalene with a m.p. of 203°C dissolved in 80 cc of alcohol are hydrogenated with 10 g of a nickel catalyst at 120–130°C under a hydrogen pressure of 400 atm until 1 mol of hydrogen is taken up. Hereby 17.5 g of the aminoalcohol with a b.p. of 206°C at 0.4 mm Hg in a yield of 79% of the theory are obtained. The hydrochloride has a m.p. of 183°C.

EXAMPLE 5.—7-methoxy-1-oxy-2-(N-tetrahydroisochinolyl)-1,2,3,4-tetrahydronaphthalene

23.5 g of the hydrochloride of the 7-methoxy-1-oxo-2(N-tetrahydroisochinolyl)-1,2,3,4-tetrahydronaphthalene with a m.p. of 195°C dissolved

in 85 cc of alcohol are hydrogenated with 20 g of a nickel catalyst at 110°C under a hydrogen pressure of 300 atm. 20.2 g of the hydrochloride of the aminoalcohol with a m.p. of 214°C in a yield of 86% of the theory are obtained.

EXAMPLE 6.—6-methoxy-1-oxy-2-N(6-methoxy-1-methyl-1,2,3,4-tetrahydroisochinolyl)-1,2,3,4-tetrahydronaphthalene

23.7 g of the hydrochloride of the 6-methoxy-1-oxo-2-N(6-methoxy-1-methyl-1,2,3,4-tetrahydroisochinolyl)-1,2,3,4-tetrahydronaphthalene with a m.p. of 191°C (m.p. of the base 130°C) dissolved in 60 cc of alcohol are hydrogenated with 0.7 g of platinum oxide at 95–100°C under a hydrogen pressure of 110 atm. 19 g of the aminoalcohol with a m.p. of 110°C in a yield of 88% of the theory are obtained. The hydrochloride has a m.p. of 208°C.

GEORG SCHEUING.
BRUNO WALACH.

ALIEN PROPERTY CUSTODIAN

COAGULATION OF EMULSIONS OF ORGANIC FILM-FORMING MATERIALS

Otto Bächle, Leverkusen - Schlebusch II, and
Gustav Sinn, Opladen, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed October 24, 1940

The present invention relates to a process for coagulating organic film-forming materials from aqueous emulsions thereof by heat.

It is known that natural latex can be rendered sensible towards heat by the incorporation therewith of mild coagulating agents. Such auxiliary agents are, for instance, ammonium or alkali metal salts either alone or in the presence of zinc salts. Natural latex having dissolved therein such agents is stable in the cold and coagulates on heating. Owing to such properties, such latices are made use of for the preparation of dipped goods, films, spongy rubber, rubber threads and the like. Earth alkali metal salts, for instance calcium salts, have also been proposed for the purpose in question. However, such agents suffer from the disadvantage that the lower and the upper limit of the permissible amount thereof must be carefully controlled if a premature coagulation is to be avoided and, on the other hand, a satisfactory coagulating effect is to be achieved in the heat. Generally spoken, there is still a lack of heat-sensibilizing agents which allow one to store such latices for an indefinite period of time without inducing the danger of a premature coagulation and, on the other hand, secure a good coagulation effect in the heat. As to the emulsions of other organic film-forming materials, for instance, those prepared by the emulsion polymerization of butadienes-1.3 or of mixtures of butadienes and other copolymerizable compounds or from polymerizable vinyl compounds or mixtures thereof, up to the present no satisfactory heat-sensibilizing process has been developed at all. Thus, alkali or ammonium salts if incorporated within such emulsions either exert no coagulating effect at all or, if employed in a higher concentration, result in a premature coagulation at ordinary temperature.

It is, therefore, the object of our present invention to do away with these disadvantages and to develop a heat-sensibilizing process for emulsions of organic film-forming materials which secures a better stability of the emulsions in the cold without impairing their capability of being coagulated in the heat. Another object of our invention resides in that emulsions of other film-forming materials than natural rubber are rendered suitable for the purpose in question. Still another object of our invention is to be seen in the preparation of molded articles, dipped goods, spongy rubber, rubber threads and the like from such emulsions.

With these and other objects in view our invention in its broadest aspect comprises dissolving a water-soluble, highly active coagulating agent within an aqueous emulsion of an organic film-forming material having incorporated therewith a water-soluble product of the interaction

of a 1.2-alkylene oxide upon a hydroxy compound, an amine or carboxylic acid, which have an aliphatic radical of at least 8 carbon atoms, and heating the emulsion to a temperature at which the said alkylene oxide reaction product becomes insoluble in water. The emulsion and the highly active coagulating agent must be chosen in such a manner that in the absence of the said alkylene oxide reaction product the former would be precipitated by the latter. In general, such emulsions are chosen as are capable of being coagulated by calcium chloride. The invention is based upon the discovery that the condensation products of the character described exert an excellent stabilizing effect upon such aqueous emulsions even towards highly active coagulating agents and that this stabilizing action gradually decreases with an increase of temperature. This effect is probably due to the fact that the said alkylene oxide-condensation products are better soluble in cold water than in hot water. Emulsions containing such alkylene oxide-condensation products and highly active coagulating agents can be stored at room temperature for a practically indefinite period of time without any premature coagulation. This is also true in the case of rubber latex or of emulsions of synthetic rubber-like materials having incorporated therewith filling materials, vulcanizing agents, vulcanization accelerators and the like. The viscosity and workability of the emulsions is not materially increased by the dissolution therein of the said auxiliary agents. In consequence thereof, our new process is very suitable for the preparation of molded articles, dipped goods, spongy rubber, rubber threads and the like. This is true in the case of natural latex as well as in the case of aqueous emulsions of other organic film-forming materials most of which could not be worked according to such heat-sensibilizing processes up to the present.

Turning now to our new invention in detail, we prefer ethylene oxide-condensation products though products derived from other 1.2-alkylene oxides such as glycidic are by no means excluded. The amount of the 1.2-alkylene oxide must be such as to impart solubility in water to the water-insoluble hydroxy compounds, carboxylic acids or amines. Besides pure aliphatic hydroxy- or amino compounds or pure aliphatic carboxylic acids, there can also be employed the corresponding alkylated aromatic compounds such as isododecylphenol. A preferred higher aliphatic compound is oleyl alcohol, the preferred condensation product being obtainable from 1 mol of oleyl alcohol and 20 mols of ethylene oxide. Products of the interaction of alkylene oxides and amines or carboxylic acids yield more homogeneous coagulates whereas the stabilizing action is the best in the case of the alcohol condensation

products. As a matter of fact, mixtures of various stabilizing agents of the character described can also be employed.—Besides natural rubber there can be employed emulsions of every kind of organic film-forming materials. The term "film-forming" is intended to cover all such materials as are capable of forming on coagulation a coherent film, either porous or homogeneous. Such compounds are, for instance, the latex-like products of the emulsion polymerization of butadiene hydrocarbons or halogen containing butadienes or of mixtures of such butadienes and other copolymerizable compounds. Furthermore, there can be employed emulsions of other non rubber-like polymerization products such as polyvinyl esters, polystyrene, polyacrylic acid esters, polyisobutylene and of mixed polymerizates of such compounds.—As highly active coagulating agents, we prefer to employ salts of polyvalent metals, for instance, water-soluble mineral acid salts of earth alkali metals such as calcium or of aluminium. Furthermore, there can be employed strong acids such as hydrogen chloride.—As a matter of fact, the emulsions may contain various other modifying agents, such as softeners, filling materials, pigments and the like and also (in the case of vulcanizable materials) vulcanizing agents, vulcanization accelerators; anti-perishing agents and the like.

The emulsion polymerizates of the character defined in the foregoing paragraph must be prepared in the presence of protective colloids or of an emulsifying agent. As the alkylene oxide condensation products represent excellent emulsifying agents, these emulsions may contain such condensation products from the very beginning. It is pointed out that in this case the additional incorporation within the emulsion of such alkylene oxide condensation products can be dispensed with.

Our invention is furthermore illustrated by the following examples, without, however, being restricted thereto, the parts being by weight, unless otherwise stated.

Example 1

156.0 ccms of a 32% emulsion of a mixed polymerizate from butadiene-1.3 and acrylic acid nitrile (75:25) are mixed while stirring with a 20% aqueous solution of an emulsifying agent which has been prepared from 1 mol of oleyl alcohol and 20 mols of ethylene oxide, and with a calcium chloride solution as precipitating agent. The following table illustrates the influence which is exerted upon the temperature of coagulation by the concentration of the stabilizing agent and of the calcium chloride, the temperature being raised for about 15°C per minute:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% CaCl ₂ -solution	Coagulation-temperature
		Degrees
7.5	10	45
10.0	10	62
12.5	10	70
15.0	10	79
7.5	20	37
10.0	20	50
12.5	20	65
15.0	20	76

Similar results are obtained by the use of ethylene oxide-octyl alcohol-condensation products or of condensation products prepared from glycide.

Example 2

In case the calcium chloride of example 1 is replaced by aluminium chloride, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% AlCl ₃ -solution	Coagulation-temperature
		Degrees
10.0	10	45
12.5	10	55
15.0	10	65

Example 3

In case the emulsion of example 1 is replaced by 187 ccms of a 26.6% emulsion of a mixed polymerizate from butadiene and acrylic acid nitrile (50:50), the following figures have been obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% CaCl ₂ -solution	Coagulation-temperature
		Degrees
10.0	20	42
12.0	20	56
15.0	20	63

Example 4

In case in example 3 AlCl₃ is used as precipitating agent, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% AlCl ₃ -solution	Coagulation-temperature
		Degrees
10.0	10	25
12.5	10	35
15.0	10	45

Example 5

In case in example 1 172 ccms of a 29% emulsion of a mixed polymerizate from butadiene and styrene (75:25) are used as latex, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% CaCl ₂ -solution	Coagulation-temperature
		Degrees
7.5	10	39
10.0	10	50
12.5	10	63
15.0	10	72
10.0	20	50
12.5	20	62
15.0	20	72

Example 6

In case in example 5 AlCl₃ is used as precipitating agent, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% AlCl ₃ -solution	Coagulation-temperature
		Degrees
12.5	10	44
15.0	10	56

Example 7

In case in example 1 100 ccms of a 50% natural latex are employed, the following figures are found:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 10% CaCl ₂ -solution	Coagulation-temperature
		Degrees
1.5	20	63
2.5	20	63
5.0	20	63
7.5	20	67
10.0	20	70
12.5	20	75
15.0	20	77

Example 8

15 parts of a 20% solution of a condensation product of isooctylphenol with ethylene oxide and 40 parts of a 20% solution of calcium chloride are added to 330 parts of a 30% aqueous dispersion of a mixed polymerizate from butadiene and acrylic acid nitrile containing as dispersing agent sodium isobutyl-naphthalenesulfonate. When warmed, this latex mixture coagulates completely. A mold which is kept at a temperature of about 100°C, when dipped into this mixture, is covered in the course of 1 minute with a film having a strength of about 0.5 mms.

Example 9

To a latex mixture containing besides vulcanization additions also filling and plastifying agents and having the following composition:

	Parts
A mixed polymerizate from butadiene and acrylic acid nitrile in the form of a 30% latex	100.00
Dibenzyl ether	2.50
A condensation product of 1 mol of oleic acid with 20 mols of ethylene oxide	1.00
A 20% aqueous solution of a condensation product of ethylene oxide with oleyl alcohol	18.50
A 85% sulfur	3.00
Zinc oxide	5.00
Caolin	10.00
Piperidine pentamethylenedithiocarbamate	0.30
Hexahydroaniline cyclohexylethyldithiocarbamate	0.30
A 5% solution of the sodium salt of a condensation product of naphthalene sulfonic acid with formaldehyde	40.00

are added 40 parts of a 10% calcium chloride solution. The mixture which, in the absence of calcium chloride, is stable to the influence of heat, coagulates after the addition of calcium chloride at about 65°C. The mixture may be stored at room temperature for many days. When dipping hot molds into the latex mixture or when heating the latex mixture in molds, coatings of a considerable strength are obtained. When extruding the emulsion through a heated nozzle, a uniform and smooth rubber thread is obtained.

Example 10

In case in example 1 aluminium chloride is em-

ployed as emulsifying agent, the following figures have been obtained:

5.

10.

15

20

Ccms of a 20% solution of the emulsifying agent	Ccms of a 10% AlCl ₃ -solution	Coagulation-temperature
		Degrees
7.5	10	56
7.5	7.5	72
7.5	5	90

Example 11

80 ccms of a 60% natural latex are mixed with a 10% aqueous solution of a condensation product of 1 mol of stearic acid and 13 mols of ethylene oxide while stirring and with a CaCl₂-solution as precipitating agent.

25

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Ccms of a 10% solution of the emulsifying agent	Ccms of a 10% CaCl ₂ -solution	Coagulation-temperature
		Degrees
2.5	5	33
5.0	5	30
7.5	5	28
10.0	5	30
12.5	5	32

Example 12

35

In case in example 11 78 ccms of a 32% emulsion of a mixed polymerizate from butadiene and acrylic acid nitrile (75:25) are used as latex, the following figures are obtained:

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45

Ccms of a 10% solution of the emulsifying agent of example 11	Ccms of a 10% CaCl ₂ -solution	Coagulation-temperature
		Degrees
10.0	5	50
12.5	5	55
15.0	5	62

Example 13

40 ccms of a 60% natural latex are mixed with a solution consisting of 40 parts of a 10% solution of a condensation product of 1 mol of stearic acid with 13 mols of ethylene oxide and 10 parts of a 20% solution of a condensation product of 1 mol of oleyl alcohol and 20 mols of ethylene oxide.

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70

Ccms of the above-mentioned solution of the emulsifying agent.	Ccms of a 10% CaCl ₂ -solution	Coagulation-temperature
		Degrees
1.25	5	32
2.50	5	52
5.00	5	63
7.50	5	62
10.00	5	60

Example 14

75

In case in example 13 a mixture of a 60% natural latex and a 32% emulsion of butadiene and

acrylic acid nitrile (75:25) is used as latex, the following figures are to be formed:

Cems of the solution of the emulsifying agent of example 13	Cems of a 60% natural latex	Cems of the 32% mixed polymerizate latex	Cems of a 10% CaCl ₂ solution	Coagulation-temperature
10	67	31	10	Degrees 46
10	50	62	10	42
15	33	93	10	50
15	16.5	124	10	40

In this case, especially smooth films are obtained.

Example 15

78 parts of a 32.2% latex of a mixed polymerizate from butadiene and acrylic acid nitrile in the proportion 75:25 are mixed with the solution of a stearylamine-ethylene oxide-condensation product and calcium chloride in the quantities as indicated in the following table, whereupon the following temperatures are obtained:

Parts of a 10% solution of the stabilizing agent	Parts of a 10% solution of the coagulating agent	Coagulation-temperature
15	5	Degrees 65
17.5	5	72
20	5	77

Example 16

50 parts of a butadiene-acrylic acid nitrile-mixed polymerizate (in the proportion 6:4) in the form of a 30% latex,
50 parts of natural rubber in the form of a 60% latex are heated with
3 parts of colloid sulfur,
10 parts of active zinc oxide,
0.6 parts of zinc phenylethylthiocarbamate as accelerator, the three last-mentioned components being dispersed in
10 parts of a 5% solution of the sodium salt of a condensation product of naphthalenesulfonic acid and formaldehyde.
25 parts of the mixture of emulsifying agents according to example 13 and
30 parts of a 10% calcium chloride solution are added thereto.

When dipping hot molds into this sensibilized mixture, strong vulcanizable films are obtained.

Example 17

50 parts of the mixed polymerizate of example 16 in the form of a 30% latex and
50 parts of natural rubber in the form of a 60% latex are mixed with a dispersion of sulfur, zinc oxide and the accelerator of example 16.
20 parts of the solution of an emulsifying agent consisting of 40 parts of a 20% solution of a condensation product of 1 mol of stearylamine and about 5 mols of ethylene oxide and 10 parts of a 20% solution of a condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide are added thereto. To this mixture,
50 parts of a 10% calcium chloride solution are added.

When dipping hot molds into this mixture, strong films are obtained which, after washing with water and drying, are vulcanized.

Example 18

As emulsion there have been used: 80 parts of a 25% emulsion of a mixed polymerizate of 66% acrylic acid methylester, 22% vinylisobutylether and 12% styrene. Upon the addition of stabilizer and of calcium chloride the following figures have been obtained:

Parts of a 20% aqueous solution of the condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide	Parts of 10% CaCl ₂	Coagulation-temperature
1	10	Degrees 45
2	10	70
4	10	83
6	10	86
8	10	89
10	10	90

Example 19

In case 80 parts of a 30% polystyrene emulsion are used, the following results have been obtained:

Parts of a 20% aqueous emulsion of the condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide	Parts of a 10% CaCl ₂ solution	Coagulation-temperature
5.0	10	Degrees 45
6.0	10	55
6.5	10	85

Example 20

In case a polystyrene emulsion is employed for the manufacture of molded articles, plastifying agents are suitably added to the mixtures to be sensibilized. These plastifying agents have the effect that the coagulate does not form a crumbly mass, but a homogeneous product. In the table mentioned below, dibutylphthalate is employed by way of example, a 20% solution of the condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide being used for emulsifying the same and for stabilizing the mixture.

Parts of a 20% aqueous solution of the condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide	Parts of dibutylphthalate	Parts of a 10% CaCl ₂ solution	Coagulation temp.
5	2.5	10	Degrees 85
5	5.0	10	83
5	10.0	10	85

OTTO BÄCHLE.
GUSTAV SINN.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF FAT AND OIL ADAPTED FOR HUMAN CONSUMPTION

Arthur Imhausen, Witten/Ruhr, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed October 24, 1940

The present invention relates to a process for the production of fat and oil adapted for human consumption or alimentary purposes.

As is well known, fats and oils adapted for human consumption are produced by subjecting 5 to a refining raw oils and fats which have a certain amount of free fatty acids. This refining consists in this that the free acids either are distilled off or are dissolved by means of a lye or other alkaline compounds. Both these methods 10 may also be combined. This method is followed by bleaching and deodorizing. In carrying out this method a certain amount of the neutral oil is lost, because this portion of oil remains absorbed in the soap-stock i. e. in the saponified fatty acid. In the production of fats adapted for 15 human consumption a portion of the raw fat always is withdrawn from the nutrition sector.

On the other hand there are oils and fats which, owing to their high content on free fatty acid and 20 their color respectively, cannot be further refined in accordance with the above mentioned methods, because the losses on neutral oil would be too high and the color cannot be removed.

Here the new method according to the invention starts. This method consists in first subjecting fats, independent on their content on free fatty acids, to a decomposition into fatty acids and glycerins. If necessary the fatty acid may then, for instance due to its dark color, be subjected to a distillation method. Then the fatty acid is esterified with glycerin again. The resulting fat which contains a small percentage of free fatty acid only may then be refined in accordance with the usual methods. The resulting refining-fatty acid may subsequently be decomposed, distilled and again esterified. In this manner all the fats which hitherto could not be refined to fat adapted for human consumption may be treated to obtain fat for alimentary purposes which is very important from an economical point of view.

So for instance palm oils, having a relatively

high content on free fatty acids, may be converted into fats adapted for human consumption in accordance with the method forming the subject matter of the invention. Tallow and similar fats of a quality and color, rendering impossible their conversion into fats adapted for human consumption by ordinary methods, now may be treated in accordance with the invention. It is known per se to decompose and distil fats. Esterifications also have already been described. By the use and suitable combination of these methods it has, however, never been tried to obtain the particular technical effect consisting in producing fats adapted for human consumption which are 15 free of objections.

It is an advantage of the new method that substances as for instance proteins or their derivatives, undigestible accompanying substances and the like influencing the conservation of the fats, may be removed, when carrying out this method, for instance by the distillation step or by other operations.

Examples

(1). 1000 kgs of palm oil, having a content on 25 free fatty acids of 30%, are decomposed. The 950 kgs of palm oil-fatty acids obtained are distilled in a vacuum. 100 kgs of this distillation-fatty acid are then esterified in a vacuum with 14 kgs of glycerin to obtain a neutral fat. The neutral fat may then be refined in accordance with the usual methods. 102 kgs of fat, adapted for human consumption and 3 kgs of soap-stock fatty acids result which latter again may be distilled and esterified. 30

(2). Dark tallow, having a content on free fatty acids of 16%, is decomposed and the fatty acid obtained is distilled, while the glycerin water is purified, evaporated and distilled, 100 kgs of the fatty acid together with 12 kgs of glycerin of 30° 35 Bé are esterified in a vacuum, whereby catalyzers, for instance tin, may be added. The ester produced is then refined as usual. 40

ARTHUR IMHAUSEN.

ALIEN PROPERTY CUSTODIAN

PREPARATION OF FATS AND OILS ADAPTED FOR HUMAN CONSUMPTION

Arthur Imhausen, Witten/Ruhr, Germany; vested in the Alien Property Custodian

No Drawing. Application filed October 24, 1940

The object of the present invention is the preparation of fats and oils adapted for human consumption from synthetic fatty acids which have been produced from suitable hydrocarbons. All paraffin and paraffin-like compounds of aliphatic nature may be used in which aromatic substances, naphthenes and the like, are not present or have previously been removed, as for instance petroleum-paraffin, hydrogenated low burning paraffin, hydrogenation products of carbon oxides and the like. Fatty acids of a very brought band, i. e. fatty acids extending from about C₄ to C₂₂ are produced. According to whether solid fats or oils adapted for human consumption are to be prepared, higher or lower portions are used, for the production of oil, adapted for human consumption, for instance, the portions from C₄ to about C₁₂ are used, whereas, for solid fats, adapted for human consumption, substantially the acids from C₁₀ to C₂₂ atoms in the carbon chain of the molecule are employed.

The fatty acids are esterified with glycerin in a vacuum which in accordance with known methods preferably may be effected with the addition of catalyzers, for instance zinc etc. After esterification the fat, however, is not yet ready for human consumption. If fats used for human consumption are produced from natural oils and fats, a deodorizing is effected which removes the odor-and taste carriers. This also is the case with fats which are obtained by esterification of olive oil-fatty acids, as is the practice for instance in the countries of the Mediterranean Sea. The undesired accompanying bodies of the fat produced from synthetic fatty acids, however, differ from these in many respects. In connection with synthetic fats, deodorizing in the ordinary sense and at the ordinary times is not effective in obtaining the purpose aimed at.

Now, it has been recognized that the purpose aimed at, i.e. the production of synthetic fats adapted for human consumption and free of taste, may be obtained, if the damping is carried out until compounds are no longer present which have an ester number. The invention, therefore, consists in a method for the production of oils and fats, adapted for human consumption, by esterification of fatty acids, obtained by the oxidation of hydrocarbons, with glycerin and subsequent refining of the raw ester, said raw fats being subjected to a distillation which in accordance with the present invention is continued until sampling after saponification, extraction with ether of the small portions of the unsaponifiable substances and decomposition of the soap

with a mineral acid result in a fatty acid the ester number of which is practically 0. Under these compounds, of course, not the glycerin ester of the synthetic fatty acids is to be understood but those compounds having an ester number which partly results from the production of the synthetic fatty acid and partly are formed later on. These substances are for instance aldehydes, ketones, lactones, estolides and, moreover, esters of fatty acids with aliphatic alcohols.

The tests, whether a fat adapted for human consumption has a "foreign ester number" is carried out as follows:

The fat is saponified, the small portions of the unsaponifiable substances are extracted with ether and the soap is decomposed with deluted mineral acid. Of the fatty acids so obtained the ester number is determined. In accordance with the invention it must be 0 or about 0. Hitherto the quality of fats adapted for human consumption has been judged or estimated according to taste and odor. As is evident, however, these characteristics are rather individual. Therefore, the fact of having found a clear characteristic for the quality of a synthetically produced fat, adapted for human consumption, must be considered a great advance in the art.

Examples

(1). Raw fatty acids which have been produced from carbon oxide-hydrogenation products by oxidation with molecular oxygen are subjected to a fractionated distillation. The portions boiling between about 150 to 280° C (2 to 5 mm vacuum) are separately caught.

100 kgs of these distillate-fatty acids are esterified with 15 kgs of glycerin in a vacuum vessel, whereby, in accordance with the boiling limits of the fatty acids, temperatures up to about 240° C are required. For the purpose of acceleration ½% of zinc powder is added. When an acid number of about 3 is obtained, a damping is effected. The latter is continued until a sample of a fat, adapted for human consumption, shows that besides the glycerin ester of the fatty acids no compounds are contained therein which also have an ester number. The fat then is refined in the usual manner with alkali, filtered and preferably again subjected to a damping. The method may also be so carried out that the first damping is not continued until the disturbing secondary compounds are completely removed, but that the last rest of these compounds is removed by the second damping.

The fat obtained is a light, solid fat adapted

for human consumption which has an agreeable taste without any odor. In a comparison test the same fatty acid ester was dampened for a shorter period of time so that a residual ester number of 3 was still present in the fat adapted for human consumption. This fat had a disagreeable harsh taste.

(2). Raw fatty acids of products of low temperature hydrogenation of low boiling products obtained by oxidation are subjected to a vacuum distillation and the portions having a carbon number of about C₄ to C₁₂ are separately caught.

100 kgs of this fatty acid are esterified in a vacuum still with 22 kgs of glycerin until an acid number of 5 is obtained. The ester then is refined with a lye and treated with bleaching earth. The ester thereupon is introduced into a damping apparatus in which finely distributed superheated steam is introduced in the fat in a vacuum. Hereby the disagreeable secondary compounds are distilled off. Damping is carried out until the ester number 0 is obtained.

ARTHUR IMHAUSEN.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR DIRECTLY OBTAINING BENZENE HYDROCARBONS FROM COAL

Bernard Juettner, Essen (Ruhr), Germany;
vested in the Alien Property Custodian

No Drawing. Application filed October 28, 1940

This invention relates to a process for directly obtaining benzene hydrocarbons from coal, without resorting to the hitherto required roundabout step of applying the coking process, and increasing to a multiple the yield, relative to the coal, of such products.

It is known partly to decompose mineral and brown coal and their transformation products by treating them with oxidizing agents in an alkaline medium. This treatment substantially yields water insoluble humic acids and their decomposition products from which certain amounts of benzene hydrocarbons may be obtained by subjecting them to a corresponding subsequent treatment. The yields thus obtainable are, however, extraordinarily small and amount, as a rule, to less than 3% of the coal, so that it is not possible to obtain benzene by this method in an economically satisfying manner.

It has further been attempted to decompose brown coal by treating it with nitric acid for a short time, whereby nitrohumic acids and nitrophenols besides a very slight quantity of benzene-carboxylic acids were recovered. This process is therefore unsuited for obtaining benzene.

Efforts have also been made to break up mineral coal by treating it with diluted nitric acid, and it was found that in this manner a certain percentage of the coal can be decomposed to form soluble oxidation products. Owing to its low yield, this procedure, too, is not adapted for the economical recovery of benzene.

The invention is based on the knowledge that, by choosing corresponding conditions, it is possible when working in an acid medium to bring not merely a fraction of the coal but the entire quantity thereof into solution and to convert it into a product from which a high yield of benzene hydrocarbons is technically obtainable in economical manner. For this purpose, the coal is decomposed according to the invention in an acid medium with the aid of oxidizing agents in such manner as to produce, above all, water soluble low-molecular cyclic carboxylic acids.

To bring about this effect the treatment with oxidizing agents of suitable concentration is carried out in the heat and so as to withdraw the products that have gradually or continuously passed into solution from any further action of the oxidizing agents and to continue decomposition under these conditions until as large a portion as possible of the initial substances has passed into solution.

This procedure prevents further decomposition of those substances that have passed already into solution by the action of the oxidizing agent and exposes to this action only the residue. The decomposition products are then subjected to a treatment with alkali under pressure, which is similar to the well-known decarboxylation proc-

ess, though in this instance larger molecules are split up also, and are thus in a very simple manner converted into a product which contains benzene hydrocarbons up to 20% of the coal with slight admixtures of other aromatic hydrocarbons besides nitrogen bases like pyridine and chinoline, phenols, etc., while simultaneously gaseous cleavage products, as methane and hydrogen, accrue. Oxidizing agents of any desired kind, as air, oxygen, ozone, peroxide, acids rich in oxygen, etc., may be used in decomposition, though the employment of acids rich in oxygen is particularly advantageous, since they are also remarkably effective oxidizing agents. The oxidizing agent should be chosen as to its nature and degree of concentration with respect to the quality of the coal to be treated and the purpose in view, i.e., to obtain therefrom a decomposition product consisting chiefly of water soluble low molecular carboxylic acids.

A very suitable oxidizing agent is nitric acid having a concentration of between 1 and 15 N.

There is no noteworthy consumption of oxidizing agents, which is particularly due to the fact that an oxidizing agent after its separation from the oxidation product may be regenerated in a very simple manner and then returned to the cycle for further use during decomposition.

The decomposition is preferably performed in two or more stages with the aid of oxidizing agents of different concentration or composition, because the reaction would be too violent if the starting material were to be subjected immediately to the action of an oxidizing agent showing a comparatively high degree of concentration. This arrangement makes it possible, moreover, to influence the composition of the intermediate products, which is particularly advantageous, since it may be necessary or desirable at times to reduce the benzene yield, for instance by the initial employment of weaker oxidizing agents or by carrying out oxidation under more preserving conditions, and to produce a correspondingly higher share of decomposition products which are not so far decomposed or are higher molecular and the treatment of which will yield therefore less benzene and more higher hydrocarbons.

Decomposition may be accelerated, possibly also while reducing the concentration of the acid used, by applying increased pressure.

In further development of the invention it has been found that the yields of benzene resp. generally benzene hydrocarbons obtained in the manner described can be substantially increased by subjecting the coal to a preliminary oxydation in a gaseous or liquid oxydizing medium. Hereby in the final result the chemical oxydation of the coal is obtained in much easier and more perfect manner.

The most simple and probably optimal kind of

performing this preliminary oxydation consists in heating the coal in the presence of air or other oxydizing gases such as oxygen or nitrogen oxydes.

The effect of this preliminary treatment is the better the higher the temperature of heating is so that it is recommendable to perform this heating under conditions which besides lower the danger of ignition of the coal i.e. to work in a thin layer preferably even in suspension or f.e. in a rotating drum.

Instead in a gaseous medium the preliminary oxydation can also be performed in a liquid oxydizing medium by a treatment f.e. with sulphuric acid under heat f.e. at a temperature of 180° C one hour. Thereafter the sulphuric acid is washed out and the coal dried and further treated in the manner described above.

Certain, however, generally not equal good results are also obtained if the preliminary heating is performed in the absence of air resp. oxygen. Also by such a treatment a certain decomposition is obtained which facilitates the further treatment according to the new process.

Besides it is possible and recommendable to apply the oxydation resp. preliminary treatment described to the residues of the single steps of the general process to prepare them for a further treatment in the next stage. Such an intermediate oxydation in a gaseous or liquid medium ameliorates in the same way the conditions for the next stage.

Besides giving a very high benzene yield, the process according to the invention affords the added economic advantage of yielding on a large scale valuable solid, liquid and gaseous by-products, particularly phenols, pyridine, chinoline, hydrogen and methane.

If the decomposition is performed in different stages and at different concentrations of the oxidizing agent or with oxidizing agents having a different composition in the various stages, fractions of different composition will result which under certain circumstances may be separately subjected to further treatment so as to increase or vary the share of other aromatic hydrocarbons obtainable besides benzene under the new process by the decomposition of these intermediate products.

Higher molecular oxidation products developed during single- or multi-stage decomposition are converted into valuable products, when splitting up under pressure occurs, by the application of an excess of alkali.

The following examples are intended merely to illustrate the application of the new process and are not limitative in character.

Example 1

100 g. mineral coal ground to 400-mesh fineness and containing 75 g. carbon are boiled for 24 hours with 8 times the amount of 2 n nitric acid, whereupon the solution is separated and the residue is boiled for several days with 5 times the

quantity of 5 n nitric acid and the dissolved portions are repeatedly removed until almost everything has passed into solution. The solutions obtained at the various steps are combined, thickened by evaporation and dried, and yield 91 g. residue chiefly consisting of polycyclic carboxylic acids. The 91 g. dried acids are then subjected to pressure for 3 hours at 450° C. and 300 metric atmospheres above atmospheric pressure in the presence of 135 g. sodium hydroxide and 120 g. water. The contents of the hot autoclave are then blown off into a receiver with cooled diluted sulfuric acid, whence the volatile matter is driven by superheated water vapor into a burette. In this way 21 g. benzene hydrocarbons are obtained which chiefly comprise benzene, toluene and xylene and slight amounts of diphenyl. The water vapor distillate contains 2 g. volatile phenols and the residue from distillation 2 g. difficultly volatile hydrocarbons and phenols besides 1.2 g. pyridine. The total yield amounts therefore to 26.2 g. aromatic substances to which must be added a certain quantity of volatile fatty acids previously produced during oxidation.

Example 2

100 g. mineral coal, as specified in Example 1, are filled with 800 cu.cm. water containing 20 cu.cm. hydrochloric acid in an acid-proof pressure vessel. At a temperature of 250° C. air enriched by oxygen is blown through, the pressure being kept below 100 atmospheres above atmospheric pressure by blowing. The solution is continually drawn off through an immersion filter and water replaced accordingly. After a period of 80 hours almost all the coal has passed into solution. 80 g. oxidation products were obtained after boiling down and treated under pressure with alkali. The yield comprised 18 g. benzene hydrocarbons and 4 g. phenols and difficultly volatile hydrocarbons.

Example 3

100 g. mineral coal as specified above were filled with 500 cu.cm. water in an autoclave, whereupon nitrous gases diluted with air were pumped through and the reaction temperature was gradually raised to 150°C and a pressure of 20 atmospheres excess pressure was maintained by reduction. The outgoing gas mixture was freed from carbonic acid and returned to the autoclave. As in Example 2, the solution was continually discharged through an immersion filter and the water replaced. After 48 hours the coal was fully dissolved. Boiling down yielded 90 g. oxydation products which on being subjected to pressure gave 20 g. benzene hydrocarbons, 4 g. phenols and difficultly volatile hydrocarbons and 1.5 g. pyridine.

In the case of all these examples it is preferable to make use of the preliminary resp. intermediate oxydation by heating in an oxydizing medium or an acid treatment.

BERNARD JUETTNER.

ALIEN PROPERTY CUSTODIAN

METHOD OF INCREASING THE VISCOSITY OF POLYMERS

Eduard Kalb, Munich, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed October 30, 1940

Various methods are known for regulating the molecular weight of polymerized unsaturated compounds manifested by the viscosity of its solutions under special conditions. F. i. higher viscous polymers are obtained by polymerizing undiluted monomers as if starting from their solutions. The grade of polymerization is reduced much more already by small additions of substances as aldehydes, ketones and the like which have a specific influence on the course and the manner of the process of polymerization than by diluting with solvents. The grade of polymerization is the higher the fewer catalysts are allowed to act and the polymers obtained only by exposure to light or by irradiation have a special position. Higher molecular polymers are further obtained by interrupting the polymerization while a considerable part of the monomers is still existing unchanged. Specially high viscous polymers are obtained above all if the polymerization is executed in emulsion, preferably in a watery one, whereby, if necessary the emulsification by any suitable emulsifying agents, preferably by partially saponified derivatives of polyvinyl alcohol, is not caused before a part of the monomers is already polymerized. The temperatures and pressures at which the polymerization is executed have also an influence on it specially if monomers of a low boiling point are applied.

Now there was found a means to increase the viscosity of the polymers under all conditions in a surprising manner. The process according to the invention principally consists in interrupting the polymerization of the monomers by cooling down if a considerable part is still unpolymerized, hereafter the thus obtained solution of raw polymers or raw emulsion is gradually heated anew until the unchanged monomer is evaporated. The time of heating must be considerably longer than that necessary for only separating the monomers.

This method is specially active if the subsequent heating is executed first for some time beneath the boiling point while the temperature is increased only later on above this boiling point whereby the pressure is gradually reduced.

The highest increase of viscosity is obtained by carrying out the subsequent heating in steps, in that way, that f.i. the temperature is kept first for some hours at 30°C, then at 40°, 50°, 70°, 90° C and about 95–100°C.

Example 1

1 kg of acetaldehyde was added to 300 kg of vinyl acetate and the vinyl compound was polymerized without an addition of a solvent until

the polymerized part of the employed monomers amounted to about 40%. Hereafter the polymerization was interrupted by cooling down. A test of the solution of raw polymers diluted by vinyl acetate until a content of polymers of 20% yielded the viscosity of 0.5–0.6 at 20°C (measured according to the method of Hercules Powder).

The solution of raw polymers was now gradually heated, always for some hours to about 30°, 40°, 50°, 70°, 90°C and finally to about 95°C whereby the pressure was gradually reduced to the technical vacuum; thereby the distillation of the monomers was completed. The total process lasted for about 20 hours. The thus obtained polyvinyl acetate the quantity of which was not increased by the subsequent heating yielded a viscosity of 4. (solution of 20%).

Example 2

300 kg of vinyl acetate were partially polymerized according to example 1 whereby only 0.2 kg of acetaldehyde were added. A solution with 20% of raw polymers showed the viscosity 4. By subsequent heating according to example 1 the viscosity was increased to 200.

Example 3

Vinyl acetate without an addition of aldehydes yielded according to Example 1 a solution of raw polymers of the viscosity 7–8 after diluting to 20%. By subsequent heating according to the above examples a polyvinyl acetate of the extraordinary high viscosity of 10 000 was obtained.

These examples show that by the method of the invention not only surprisingly high viscosities can be obtained which are connected with excellent mechanical thermal and chemical properties of the polymers but that even relatively high viscosities can be also obtained by applying auxiliary methods which would lower the viscosity but modify the polymerization in various directions. F.i. a dilution with solvents and an addition of aldehydes are not to be applied if especially high viscosities are intended, but by the excellent efficiency of the method according to the invention, it is nevertheless possible to attain relatively high viscosities when the regulating and modifying effect of these additions upon the forming polymers is also applied. Especially the known polymers, peculiarly modified by an addition of a large amount of aldehyde, may be obtained in a considerably higher molecular state. On the other hand the special polymers obtained by applying a large amount of catalysts may now

be obtained without giving up a relatively high viscosity.

By the method according to the invention it is also possible to increase considerably the efficiency of other methods which aim at high viscosities. F.i., the polymerization in emulsion in combination with the method according to the invention yields still higher viscosities than the polymerization in emulsion per se. The same is due to the polymerization effected by exposure to light resp. by irradiation or radiation.

The new method may be applied to the polymerization of all the unsaturated compounds being polymerizable to high molecular substances especially to all kinds of aliphatic or aromatic vinyl compounds and esters and derivatives of acrylic acid and interpolymers of these substances. Fundamentally, it is necessary for the

effect according to the invention that the solution or emulsion of raw-polymers being after-treated still contains a considerable amount of monomers. On the other hand also the modified polymers being formed by far-reaching polymerization of the applied monomers may be improved by this method. For this purpose monomers are added before or after the end of the polymerization. These added monomers may be the same as the polymerized one or they may be of other nature. Mixtures of various monomers may also be applied. F.i. monomer vinylacetate or acrylic acid or β -Oxydroxybutadiene and the like are added to a mixture of vinyl acids and vinyl chloride, nearly completely polymerized and then after-heating according to the invention may be applied to the modified raw polymers.

EDUARD KALE.

ALIEN PROPERTY CUSTODIAN

INTERPOLYAMIDES

Emil Hubert, Dessau-Ziebigk, and Hermann
Ludewig, Berlin S W 68, Germany; vested in
the Alien Property Custodian

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Our present invention relates to new poly-
amides and more particularly to easily soluble
interpolyamides.

It has already been proposed to prepare poly-
amides by condensing two different diamines with
two different dicarboxylic acids in substantially
equimolecular amounts. The interpolyamides
thus obtained are only partially soluble in meth-
anol or other simple aliphatic alcohols. The
solubility of these mixed condensates rarely
amounts to above 10%.

It is also known to produce polyamides from
two condensation reactants one of which con-
tains a heteratom in the carbon chain, for in-
stance a sulfur atom. Such simple polyamides
are insoluble in methanol and simple aliphatic
alcohols as attempts have shown.

An object of our present invention is to provide
interpolyamides at least 20 per cent of which
dissolve in alcohols or mixtures of alcohols and
halogenated hydrocarbons.

Another object is the preparation of adhesives,
artificial leather, and laminated articles from the
new polyamides.

A further object is the manufacture of films,
foils and coatings from said polyamides.

Other objects of our invention will become ap-
parent as the description proceeds.

These objects are accomplished by condensing
at least two α - ω -dicarboxylic acids with at least
two α - ω -diamines, at least one of these reactants
containing sulfur in the carbon chain. Instead
of one of these diamine-dicarboxylic acid com-
binations an aminocarboxylic acid may be em-
ployed and in place of the dicarboxylic acids and
diamines or the aminocarboxylic acids the amide-
forming derivatives thereof, for instance esters,
chlorides, anhydrides or lactams may be used in
the preparation of the new soluble interpoly-
amides.

The solubility properties of our new interpoly-
amides surprise all the more so as a product
which is insoluble in aliphatic alcohols is ob-
tained by condensing two salts which have the
same acid components and one salt of which is
a diamine salt containing sulfur, for instance,
such as $\beta\beta'$ -diaminodiethylsulfide-adipic acid and
hexamethylenediamine-adipic acid. The solu-
bility behavior of interpolyamides of this kind
is shown in the following Table wherein HA

means hexamethylenediammonium adipate and
DSA diaminodiethylsulfide adipate (the parts be-
ing by weight).

5	Parts of reactants HA + DSA		Parts of inter- polyamide per 100 parts of methanol	Solubility behavior
	0	100		
10	10	90	2	Undissolved.
	25	75	2	Undissolved, slightly fragile.
15	33.3	66.7	1	Undissolved, fragile.
	50	50	1	Do.
20	75	25	1	Undissolved, hard.
	85	15	1	Do.
25	100	0	2	Undissolved, slightly fragile.
			2	Undissolved, hard.

If, however, the diamine containing sulfur is
heated together with another diamine and corre-
sponding quantities of two different dicarboxylic
acids, interpolyamides are obtained of which 20-
40% are easily soluble in methanol or a mixture
of methanol and halogenated hydrocarbons.

In using two polymethylenediamine-dicar-
boxylic acid salts the mixture thereof in equi-
molecular amounts or in the proportion by weight
of 1:1 is generally very advantageous. For in-
stance, an interpolyamide prepared from hexa-
methylenediammonium sebacate and diaminodi-
ethylsulfide adipate has the best solubility be-
havior when the reactants are present in the
ratio of 1:1.

The solubility in methanol of interpolyamides
prepared from hexamethylenediammonium seba-
cate (HS) and diaminodiethylsulfide adipate
(DSA) is shown in the following Table (the parts
being by weight):

40	Parts of reactants HS + DSA		Parts of inter- polyamide per 100 parts of methanol	Solubility behavior
	0	100		
45	25	75	2	Undissolved.
	33.3	66.7	2	Swelled, nearly undissolved, partially fragile.
50	50	50	2	Dissolved nearly without residue.
	54.6	45.4	25	Dissolved without residue.
55	(Molecular proportion)		10	Do.
	66.7	33.3	2	Only a small part dissolved.
60	75	25	2	Nearly undissolved.
	100	0	2	Undissolved.

When ethylenediammonium sebacate is substituted for half the amount of hexamethylenediammonium sebacate, i. e. when the interpolyamide is produced from 50 per cent of diaminodiethylsulfide adipate, 25 per cent of hexamethylenediammonium sebacate, and 25 per cent of ethylenediammonium sebacate, the solubility of the interpolyamide is essentially increased. It is possible to prepare solutions containing 30-50 per cent of this interpolyamide.

The interpolyamides are advantageously obtained by condensing together two salts consisting of different diamines and different dicarboxylic acids. It is known of course that the components may also be caused to react separately in their molecular proportions. Instead of the free dicarboxylic acids the corresponding esters, chlorides, diamides, and semiamides may be employed and diuremethanes, diammonium formates and diammonium carbonates may be substituted for the diamines. By adding amino acids or esters and anhydrides thereof such as ϵ -caprolactam to the compositions of the salts condensation products are formed which possess an increased solubility in methanol or mixtures of methanol and a halogenated hydrocarbon.

Interpolyamides prepared from ϵ -caprolactam or 6-aminohexanoic acid and a polymethylenediammonium salt also dissolve relatively easily (20 per cent thereof) in methanol. On the other hand the solubility of condensates derived from an ω -aminocarboxylic acid of high molecular weight, for instance such as 9-aminononanoic acid or 11-aminohendecanoic acid, and a polymethylenediammoniumdicarboxylate is low (about 2-3 per cent) if the diamine used in the condensation does not contain at least one atom of sulfur in the carbon chain. Interpolyamides, however, produced by reacting an aminocarboxylic acid of high molecular weight with a diammonium salt containing sulfur comparatively easily (above 20 per cent) dissolve in methanol, ethyl alcohol, butanol, and mixtures of alcohols and halogenated hydrocarbons. By using a diamine containing sulfur the solubility of the interpolyamides which have ϵ -caprolactam as a reactant can likewise considerably be increased.

As solvents such liquids may advantageously be employed as have a high evaporation velocity, for instance, methanol, ethyl alcohol, propanol, butanol, and mixtures thereof. Moreover, mixtures of alcohols with halogenated hydrocarbons such as chloroform, carbon tetrachloride, and methylene chloride are solvents suitable for polyamides containing sulfur. Solutions of these polyamides in mixtures of alcohols and halogenated hydrocarbons also remain clear on cooling in super-cooled condition for a long time. They are, therefore, useful as ingredients in impregnating and coating compositions and as clear lacquers. When dissolved in an alcohol the polyamide tends to precipitate in most cases after some time. By adding 5-50 per cent of chloroform, chlorobenzene, cresols or other substances suitable as stabilizers the solutions can be kept in the clear condition for some days.

The solutions of polyamides of our invention are especially useful in making adhesives, laminated layers, and leather substitute. Furthermore, they are applicable when desired with additions of dyestuffs, pigments, and plasticizers in the preparation of smooth and pliable films, foils, and coats having a high tensile strength and tenacity. The following Examples in which

quantities of reagents are parts by weight illustrate our invention.

Example I

5 Equal parts of hexamethylenediammonium sebacate and $\beta\beta'$ -diaminodiethylsulfide were condensed together at 210° and 760 mm for 12 hours in an atmosphere of nitrogen. To the interpolyamide thus obtained a sufficient amount of
10 methanol was added and the mixture was heated for three hours. 25 per cent of the interpolyamide were clearly dissolved in methanol by this heating treatment. On cooling the solution became turbid after some time. The precipitated
15 interpolyamide could again readily be dissolved by heating. When 20-30 per cent of chloroform were added the solution remained clear for several days. By evaporating the solvent clear and
20 pliable films were obtained.

Example II

Equal parts of ethylenediammonium sebacate and the salt prepared from $\beta\beta'$ -diaminodiethylsulfide and adipic acid were condensed together
25 at 210° and 760 mm for 15 hours in an atmosphere of steam. To the interpolyamide thus formed was added a sufficient amount of methanol and the mixture was heated under reflux for several hours. 20 per cent of the interpolyamide
30 were clearly dissolved in methanol by this heating treatment. The solution is useful as an ingredient in coating compositions and making laminated articles.

Example III

35 50 parts of $\beta\beta'$ -diaminodiethylsulfide adipate, 25 parts of hexamethylenediammonium sebacate, and 25 parts of ethylenediammonium sebacate were condensed together at 210° and 760 mm for 12 hours in an atmosphere of nitrogen.

40 To 100 grams of the interpolyamide thus obtained were added 400 cc. of methanol and the mixture was heated under reflux for several hours. The interpolyamide completely dissolved in the methanol. The solution may be used as an
45 ingredient in impregnating compositions and making smooth and pliable foils.

Example IV

50 40 parts of hexamethylenediammonium sebacate, 40 parts of $\beta\beta'$ -diaminodiethylsulfide adipate and 20 parts of ethylenediammonium adipate were condensed together at 210° C and 760 mm for 24 hours in an atmosphere of nitrogen. To
55 300 grams of the interpolyamide thus obtained were added 600 cc. of methanol and 400 cc. of butanol and the mixture was heated under reflux for 2-3 hours until the interpolyamide was completely dissolved. The solution became turbid
60 on cooling. By adding chloroform the solution could be kept clear for many days. Solutions containing 5-10 per cent of the interpolyamide also remained clear as supercooled solutions for some time without any stabilizer.

Example V

65 50 parts of hexamethylenediamine sebacate, 25 parts of ethylenediamine adipate, and 25 parts of $\beta\beta'$ -diaminodiethylsulfide adipate were condensed together at 210° C and 760 mm for 20 hours
70 in an atmosphere of nitrogen. To 400 grams of the interpolyamide thus formed were added 1000 cc. of methanol and the mixture was heated under reflux for three hours. The solution which tended to become turbid on cooling could be kept clear
75 for several days by adding a stabilizer.

Example VI

Equal parts of ϵ -caprolactam and $\beta\beta'$ -diaminodiethylsulfide adipate were condensed together at 180° C and 760 mm for 12 hours in an atmosphere of steam. To 100 grams of the interpolyamide thus prepared were added 200 cc. of methanol and the mixture was heated under reflux until the interpolyamide was completely dissolved. The light-colored methanolic solution was a viscous liquid.

Example VII

50 parts of ϵ -caprolactam, 25 parts of hexa-

methylenediammonium sebacate, and 25 parts of $\beta\beta'$ -diaminodiethylsulfide adipate were condensed together at 180°C and 760 mm for 12 hours in an atmosphere of nitrogen. To 100 grams of the interpolyamide thus prepared were added 100 cc. of methanol and the mixture was heated under reflux for several hours. The resulting solution was clear and very viscous and is useful in the making of films and foils.

EMIL HUBERT.
HERMANN LUDEWIG.

ALIEN PROPERTY CUSTODIAN

POLYMERIC PRODUCTS AND THE METHOD FOR PRODUCING THE SAME

Hans Bergk, Krefeld, Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 14, 1940

This invention relates to polymeric products and the method for producing the same.

An object of this invention is the production of polymeric products by a novel manner.

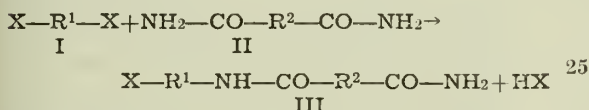
Another object of this invention is the production of a novel polymeric product.

A further object of this invention is the production of polymeric products from relatively stable substances.

A more specific object of this invention is to produce a polymeric product from the polymerization of acid amides with di-halides.

Acid amides themselves may be very easily produced in several ways, for example, from di-esters and aqueous ammonia, or from acid chloride likewise by reaction with aqueous ammonia. The halides are likewise easily produced in many ways which are known to the art.

In suitable combinations, di-halides of the type $X-R^1-X$ combine with acid amides of the type $NH_2-CO-R^2-CO-NH_2$, according to the following reaction:



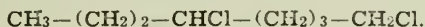
In this equation:

$X = Cl, Br, I,$

$R^1 =$ Aliphatic, aromatic or cyclic residue with straight or branched chains, and

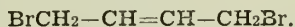
$R^2 =$ A bi-valent radical which may be of the type similar to R^1 .

The halogen may either be at the end of the chain, for example, $BrCH_2-(CH_2)_4-CH_2Br$, or in the middle, for example,



The chain may consist only of C-atoms but also may contain oxygen, sulphur or nitrogen bridges.

The chains or the side chains can also contain double bonds, for example



The radical R^1 can contain atoms or atom groups which facilitate the splitting off of the halogen atom.

The product III can either be reacted with itself or with I and II for the formation of a larger molecular chain.

The reaction can be substantially accelerated if a catalyst, for example, alkaline oxide, hydroxide or carbonates, or basic organic substances, aluminum chloride or zinc chloride are added to the reaction mix.

An additional possibility for accelerating the reaction is by the removal of the hydrogen halides

which become free during the reaction. Also an acceleration may be effected by a raising of the temperature of the mix as well by changing the pressure. The temperature should be so chosen that no decomposition of the amides will result, since, for example, in the case of adipinic acid diamides, this may happen if the mix is heated for a long time even beneath the melting point. It is best for the purposes in mind to exclude all oxidizing substances, so that the atmospheric hydrogen can be replaced by nitrogen. If it is desired to decelerate the reaction or bring it to a standstill this can be done by the removal of the catalyst in addition to the maintenance of a lower temperature, so that in the case of a supplemental heating which is necessary for a further working of the material, no further polymerization can arise.

A further advantage of the method according to this invention lies in the fact that polymerization can also be stopped by raising of the temperature of the mix and at the same time adding materials which are designed to saturate the end groups. Such materials can be combinations of the type I or type II, or materials which react with the end group, such, for example, as amides, acid chlorides and the like.

As specific examples of the method and product formed in accordance with this invention, attention is directed to the following:

Example 1

One molecule of 1,6 dibromo-n-hexane and one molecule of adipinic acid diamide are brought into solution or into the finest suspension in 2500 cubic centimeters of benzene by an extremely rigorous agitation. Being careful to exclude hydrogen and atmospheric oxygen, one adds 50 grams of the most finely pulverized aluminum chloride together with oxygen-free nitrogen. When it is desired to separate the aluminum chloride, the reaction mix can be poured into vigorously agitated water so that a minute separation and complete removal of the aluminum chloride is effected.

Example 2

One molecule of adipinic acid diamide and one molecule of dibromo butadiene are heated in an autoclave in the presence of hydrogen at 180°C until a body of the desired plastic property arises. Viscosity can then serve as a measure of this desired plasticity. The hydrogen bromide which will arise can be removed from the reaction mix by proper amount of caustic soda.

HANS BERGK.

ALIEN PROPERTY CUSTODIAN

TANNING AGENTS AND PROCESS OF PREPARING THEM

Ernst Koch, Frankfurt am Main, Germany;
vested in the Alien Property Custodian

No Drawing. Application November 14, 1940

It is known that tanning agents may be prepared by causing natural resins and aromatic hydroxy compounds to react with sulfuric acid. Either a molten mixture of the two constituents is sulfonated or a condensation product is first prepared by heating the molten mixture in the presence of dilute acid and the said product is then sulfonated.

After removal of the sulfuric acid in excess and also after mixing with synthetic tanning agents, all tanning agents obtained as above described are very sensitive to salts and are not compatible in all proportions with sulfite cellulose waste liquor or with vegetable tanning agents. In view of these properties it is in many cases impossible to use tanning agents prepared from resin and aromatic hydroxy compounds simultaneously with other tanning agents of either natural or synthetic origin.

The above mentioned two processes not only yield tanning agents with unsatisfactory properties but the processes proper have technical drawbacks. In both cases it is necessary to first melt the resin. Since the resin, however, is a bad conductor of heat and, moreover, cannot be stirred during the melting process, it is necessary to apply a considerable amount of heat and to spend much time. The subsequent sulfonation being a very exothermic reaction, the melt must be cooled to a very low degree prior to the addition of the sulfonating agent. This again involves loss of time so that the operation up to the beginning of the sulfonation requires about 50% more time than does the sulfonation process itself.

Now, I have found that tanning agents are obtained which are similar to the known products but have a much better stability to salts and a better compatibility with sulfite cellulose waste liquor and vegetable extracts, by first sulfonating the aromatic hydroxy compounds, causing the sulfonic acid to react with the resin and then sulfonating the reaction product obtained.

Furthermore, I have found that, according to the process of the present invention, it is not only possible to separately prepare the hydroxyaryl-sulfonic acid and to cause this acid to react at any time with the resin, i. e. to proceed in two separate operations wholly independent of each other but that it is advantageous to cause the resin to react with the still warm sulfonation mass of the hydroxy compound.

The reaction may be carried out as follows: the quantity of acid necessary for the sulfonation or advantageously a little less than required for complete sulfonation is caused to run into the aro-

matic compound. The temperature of the sulfonation mass rises, for instance when cresol is used, to 70°C–90°C. Thereupon, the resin is introduced in portions into the sulfonic acid, while stirring, the proportion being about 1–3 parts by weight of resin for 1 part by weight of aromatic hydroxy compound. The most favorable ratio is 2 parts by weight of resin for 1 part by weight of the hydroxy compound. By introducing the resin into the sulfonic acid, reaction of the components takes place with elimination of heat. Consequently, the resin melts at once so that it may be introduced rather quickly. Thus the heat of reaction serves to melt the resin. The whole is then cooled. It is not necessary to cool to such low temperatures as with the known processes and the quantity of acid necessary for the second sulfonation is caused to run in; thus less time is required and less cooling liquid need be applied. Also during the sulfonation no or hardly any cooling is required.

The sulfonation processes take place in known manner; advantageously there is used a small excess of the weight, used for both sulfonations, of sulfonating agent such as fuming sulfuric acid, sulfuric acid monohydrate, chlorosulfonic acid or the like calculated on the total amount of resin and aromatic hydroxy compound. The excess amounts to about 20% of the weight of the resin-phenol mixture. Also a larger excess is not detrimental. The washing out of the sulfuric acid in excess after the precipitation of the tanning agent and, if desired, the mixing of the product washed out with a synthetic tanning matter also take place according to known methods.

Generally, any supply of heat is superfluous during the whole reaction process, the time necessary until the end of the sulfonation is reduced to less than half the time hitherto required and the quantity of the cooling water amounts only to a fraction of that used according to the known processes.

It is also possible to start from ready-made sulfonated aromatic compounds. In this case the sulfonic acid must be heated to the melting temperature of the respective resin, that is to say, practically to 50°C–90°C. The resin is then introduced as above described and the second sulfonation follows.

As natural resins there may be used balsamic resins and resins obtained by extraction as well as constituents of these resins such as abietic acid, furthermore, tall oil. Suitable aromatic hydroxy compounds are phenol, cresols, xylenols, resorcinol, naphthol, dihydroxydiphenylsulfone,

dihydroxydiphenylmethane and mixtures of these substances such as crude cresol, phenol oil, creosote oil.

The following example illustrates the invention, the parts being by weight:

30 parts of sulfuric acid monohydrate are caused to run, while stirring, into 45 parts of cresol. Hereby the temperature of the sulfonation mass rises to 80°C and after a short time the mass is soluble in water. Thereupon, 135 parts of american balsamic resin HJ are introduced in portions, the whole rising to a temperature of 100°C-110° C. After stirring for a short time, the whole is cooled to about 75° C and 160 parts

of sulfuric acid monohydrate are run in. When the sulfonation is finished, the main quantity of the acid in excess is removed by washing out after precipitation of the tanning matter and the tanning matter is then rendered neutral by addition of 25 parts of aqueous ammonia of 25% strength, acidified by means of a solution of 20 parts of oxalic acid in 140 parts of water and 250 parts of a synthetic tanning matter, prepared according to patent specification No. 1,912,260 by reaction of a still liquid phenol-formaldehyde condensation product with benzylnaphthalene-sulfonic acid, are added.

ERNST KOCH.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR OBTAINING TRANSPARENT
MOLDED BODIES

Gerhard Schorsch, Brussels, Belgium; vested in
the Alien Property Custodian

No Drawing. Application filed November 22, 1940

This invention relates to a process for obtaining transparent, limpid and stable molded bodies from thermoplastic organic compounds, which process is to be used more particularly for the manufacture of denture material.

It is known that in the manufacture of molded objects from thermoplastic organic compounds by means of plaster molds, special precautionary measures are necessary for eliminating the harmful action which the water vapour escaping from the plaster during the heating of the mold, exerts upon the said thermoplastic organic compounds.

It is also known that plaster molds are of common use for producing denture material from thermoplastic substances. Among the latter substances, the following may be cited: the cellulose esters, the polymerized vinyl and styrol products, the polymerized esters of the acrylic acid and of the substituted acrylic acid (for instance the monomethacrylic acid), the phenoplastic resins.

It has also been proposed to use mixtures of entirely polymerized organic solid bodies with liquid monomeric or partially polymerized compounds which under the action of heat and pressure may be completely polymerized whereby hardening is obtained. All these mixtures are very sensitive to water vapour and practice has shown that if no special measures are taken, the molded objects instead of being transparent have a milky or opalized appearance which becomes stronger in time; moreover they are unstable and their mechanical properties are insufficient.

In order to avoid these drawbacks, various measures have been proposed, consisting for instance in a preliminary heating of the plaster mold before introducing the charge therein, or in a galvanic covering of the walls of the mold in order that the metal covering thus formed shall prevent the water vapor from reaching the charge which fills the mold.

Another process consists in lining the inner walls of the mold with a thin metal sheet before it has been filled, but the placing of a metal lining in position is a delicate, long and costly operation. Moreover, the operation is not always successful and must sometimes be renewed.

The process according to the present invention allows of avoiding all the above drawbacks and of obtaining in an easy manner, even by persons not specialized in this kind of work, molded bodies which are perfectly limpid and stable, from organic compounds of the kind above mentioned, without the necessity of applying delicate hand operations or special precautionary measures.

The invention consists broadly in adding to the

mass to be molded, comparatively small amounts of chlorinated organic substances having a high molecular weight. The addition is preferably effected before the mass is introduced into the mould. Among the substances to be used the following may be cited: chlorinated paraffins, chlorinated di-phenyl compounds and chlorinated naphthalene. My experiments have shown that such additions allow of obtaining perfectly transparent and stable molded bodies.

Among the chlorinated substances, the chlorinated diphenyl compounds give very good results. These compounds may be used, if necessary, in a mixture with other aliphatic or aromatic compounds.

The amount of substances of addition to be used may vary between very large limits and depends more particularly on the molding material used and on the conditions of its use and hardening. Entirely satisfactory results have been obtained in certain cases with amounts lower than 1% in weight of the molding charge. Generally less than ten per cent are sufficient.

It should also be noted that the resinous and wax-like properties of the chlorinated substances, as well as the thermo plastic quality of most of these substances allows of increasing at will the proportion of substances of addition, in order to take advantage of the modifications or advantages resulting from the combination of the specific properties of such chlorinated substances and of the specific properties of the molding substance itself.

The addition of substance of addition may be made at any moment during the manufacture of the thermoplastic substances, but it should preferably be effected before the molding operation. Care should be taken to obtain as homogeneous a distribution as possible of the substances of addition into the material to be molded. When this material consists of mixtures of solid, entirely polymerized compounds with monomeric liquid or/and partially polymerized compounds, which under the action of heat and pressure are capable of becoming entirely polymerized whereby hardening takes place, the substances of addition may be dissolved into the liquid compound before the latter is mixed with the solid compounds, and this allows of obtaining in a simple and particularly advantageous manner a homogeneous distribution of the substances of addition into the material to be molded.

In addition to the substances of addition above mentioned, the mixtures may be also completed by the ordinary additions, such as plastifiers, sol-

vents, waxes, paraffins, fillers, catalysers such as oxygen-liberating agents, soluble or insoluble dyestuffs, pigments, etc.

Mixtures are known which contain natural or artificial resins, for instance halogen hydrocarbons; such additions however have been proposed for improving the qualities of the mixtures themselves, but it has not been hitherto recognized that a systematic addition of organic chlorinated substances of high molecular weight, more particularly to mixtures of thermoplastic substances and substances capable of being polymerized and of becoming thermoplastic after polymerization, led to new and unexpected effects. Indeed, none of the substances previously proposed allowed of avoiding the necessity of lining the mold with a thin sheet of metal, or of taking the other precautionary measures above mentioned, and which the present invention allows of suppressing completely.

The new technical effect obtained by the process according to the present invention consists in the fact that the mass to be molded under the action of heat and pressure is made insensitive to the action of water vapor, and supplies molded objects which are resistant, limpid and stable.

Examples of carrying the invention into effect will be given hereinafter. In these examples the parts mentioned are parts in weight.

Example 1

A mixture is prepared of

Parts monomeric methacrylic ester-----	60
Parts butylacrylic ester-----	20
Parts acrylic nitrile-----	10
Parts vinyl acetate-----	10

To this mixture 0.08% of a soluble red dye and 0.01% of benzoyl peroxide may be added.

One part of chlorinated naphthalene, more particularly of the product known under the commercial name of "Halowax", and one part of chlorinated di-phenyl, more particularly of the product known under the commercial name of "Arochlor No. 4465", are also added to the mixture.

The mixture thus prepared is heated in a

double-walled mixer provided with a reflux condenser. The liquid becomes more and more viscous and after a few hours the polymerization is ended. Stirring by means of stirring blades or arms leaves the molding material in a state of grains of more or less regular shape.

This mass is used as such for filling an undried plaster mold, of the type usually employed in dental surgery, and the mold is afterwards subjected to pressure and heated until the inner temperature has reached 150° C. After cooling, the molded mass may be withdrawn.

Example 2

One part of the product known under the commercial name "Arochlor No. 4465" is dissolved into 40 parts of monomeric methyl methacrylate, and the solution thus obtained is mixed with 60 parts of pulverized and polymerized methyl ester of the methacrylic acid. The mixture is stirred and gives then a rubber-like mass which is immediately used, for instance for filling molds for dental prosthesis, made of undried and non-metallized plaster. After compression, the mold is heated in a water vulcanizer up to 130° C and at a water vapor pressure of about 4 kilos during one hour in all. After cooling, the mould may be withdrawn and cleaned in the usual manner.

The objects molded by means of the substances mentioned in the above examples are resistant, limpid and stable and do not show any trace of alteration, even after several months.

It is to be noted that although the above examples apply more particularly to the manufacture of objects to be used in the dental prosthesis, the process according to the present invention is not limited to the said manufacture but may be used broadly for obtaining molds from organic compounds of the type mentioned and with a view to obtaining resistant, limpid and stable objects.

For the molding operation, use may be made of a mixture consisting of polymerized and pulverized mono-methacrylic acid ester with partially polymerized methacrylic acid ester and with monomeric methacrylic acid ester.

GERHARD SCHORSCH.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF ARTIFICIAL RESINS

Werner Wolff, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 26, 1940

The present invention relates to a process for the manufacture of artificial resins.

It is known that artificial resins can be prepared by heating urea-formaldehyde or thiourea-formaldehyde condensation products or such substances as are capable of forming such condensation products together with finished resins from polyvalent alcohols, namely glycol or glycerine, and polybasic acids in the presence of monovalent alcohols. In order to obtain soft resins of the said type it is necessary to employ condensation products from polyhydric alcohols, polybasic acids and monobasic fatty acids, as for example linoleic acid or ricinoleic acid. The resins so obtained, however, are sensible to light and temperature.

I have now found that soft, elastic artificial resins of good power of resistance to the action of light and temperature are obtained by heating low-molecular condensation products from a urea and/or thiourea and formaldehyde or the initial substances capable of forming the said condensation products to a temperature of from 100°C to 160°C, in the presence of monohydric alcohols together with weakly acid condensation products containing free hydroxy groups and being soluble in alcohols, from aliphatic (i.e. open-chain aliphatic or cycloaliphatic) dicarboxylic acids containing from 5 to 10 carbon atoms and trivalent alcohols or alcohols of higher valency containing more than 3 carbon atoms in the molecule, until appreciable quantities of water are no longer split off, but the resulting resins are still readily soluble.

Suitable open-chain aliphatic or cycloaliphatic dicarboxylic acids with at least 5 carbon atoms in the molecule are for example glutaric acid, adipic acid, pimelic acid, ketopimelic acid, sebacic acid and cyclohexanediadic acid. Among suitable trivalent or higher valent alcohols containing more than 3 carbon atoms in the molecule may be mentioned, for example, trimethylethane, trimethylolpropane, pentaerythrite and hexanetriol. Mixtures of several of the said dicarboxylic acids and/or polyhydric alcohols may also be employed. The condensation products from the said aliphatic dicarboxylic acids and polyhydric alcohols must not be strongly acid, as otherwise premature gelatinization would occur and because strongly acid constituents are undesirable in resins to be used as a coating agent. The acid number should not be higher than about 40, preferably it should be in the range up to 30. Condensation products from the aliphatic dicarboxylic acids and the polyhydric alcohols which are faintly acid and

soluble in alcohol are obtained by heating mixtures of the initial materials at not too high temperatures, preferably at 135° to 250°C.

The low-molecular condensation products from urea and/or thiourea and formaldehyde are made by known methods, preferably in a basic medium. The simultaneous employment at this stage of a monohydric alcohol is advantageous. The condensation products or their constituents forming such products, are then heated, in the presence of a monovalent alcohol and the condensation products from the dicarboxylic acids and polyhydric alcohols aforedescribed, at a temperature of between 100° and 160°C. It is advantageous to use monohydric alcohols with a boiling point above 100°C, as the water formed in the condensation or introduced by the aqueous formaldehyde may then be removed with special ease by distillation. When appreciable quantities of water are no longer split off, the condensation is discontinued. The resulting resin is then obtained in the form of an alcoholic solution.

The resins are eminently suited for the production of baking varnishes. The coatings obtained with the said resins are very light in colour and extremely fast to temperature and light. The varnishes can be caused to dry already at ordinary or slightly raised temperatures by an addition of acid hardeners, as for example strong acids, as hydrochloric acid, formic acid, chloroacetic acid, sulphosalicylic acid and lactic acid, or acid esters, as maleic acid monomethyl ester, or substances capable of splitting off acid, as benzenesulphochloride and toluenesulphochloride. These different possibilities of effecting their drying renders it possible to use the resins in different manner in the lacquer industry. Baking varnishes prepared therefrom may be applied with special advantage for example onto metals. The varnishes are distinguished by a good adherence to light metals. By virtue of their extremely high elasticity they may even be employed for coating thin metal foils.

Materials sensible to the influence of higher temperatures may preferably be coated with the resins in admixture with one of the said acid hardeners. Thus, for example, extremely elastic coatings on wood, paper, textiles, leather and similar materials may be obtained, the products thus obtainable being useful as artificial leather, oil-cloth, oil skin (oil silk) and patent leather (japanned leather). The elasticity and the gloss of the coated products may be influenced at will by varying the proportion of the condensation products from the aliphatic dicarboxylic acids and

polyhydric alcohols and the urea- or thiourea-formaldehyde condensation products in the resins. The higher the percentage in condensation products from the said dicarboxylic acids and polyhydric alcohols, the higher generally is the gloss and the elasticity.

By baking as well as by hardening the resins in the presence of acid hardeners, the resins and hence the coatings prepared therefrom are rendered to a far-going degree insoluble in the usual organic solvents. The varnishes in the hardened condition are also distinguished by a good resistance to dilute lyes, acids and salt solutions.

The following Examples will further illustrate how the present invention may be carried out in practice, but the invention is not restricted to these Examples. The parts are by weight.

Example 1

292 parts of adipic acid are heated together with 400 parts of trimethylolethane while stirring at 250 to 280° C until about 120 parts of water are distilled off which is the case after about 1 hour. The reaction mixture is then allowed to cool and is diluted with alcohol to form an about 70 per cent solution. The acid number of the resinous product thus obtained is 9.

In a vessel provided with a reflux condenser, means for removing volatile parts by distillation and a stirring device 480 parts of paraformaldehyde and 384 parts of urea are dissolved in 2000 parts of ethyl alcohol while adding 48 parts of 25 per cent aqueous ammonia. The whole is heated for an hour under reflux and 1050 parts of the 70 per cent solution of the adipic acid-trimethylolethane resin obtained according to paragraph 1 are added. The mixture is further heated to boiling and the reflux cooling is so regulated that 1500 parts of alcohol distill off slowly together with the major part of the water formed during the reaction. Fresh alcohol is added and the removal of the water together with alcohol is continued until the mass is practically free from water. The product is then diluted with alcohol to form an about 50 per cent viscous solution which as such or after the addition of nitrocellulose, resins and other film-forming substances is suitable as an adhesive.

Example 2

110 parts of the 70 per cent alcoholic solution obtained according to Example 1, paragraph 1, are diluted with 180 parts of normal butanol. 90 parts of dimethyl urea and 15 parts of paraformaldehyde (or trioxymethylene) are added and the whole is condensed by heating for about 10 hours while distilling off alcohol, water and butanol. After adjusting the concentration of the solution to 50 per cent it is filtered in order to remove any parts causing turbidity. The solution is suitable as an adhesive and can also be employed for lacquering purposes. For the latter purpose pigments, such as titanium white, aluminium bronze and the like, may be added and the desired viscosity may be obtained by dilution. Such lacquers are suitable especially for metallic surfaces including light metal surfaces. The lacquers may be brushed or sprayed. After evaporation of the solvent the coatings obtained are preferably baked at 150° C. They possess excellent elasticity, hardness and fastness against scraping; they are very fast to light and do not yellow even at higher temperatures. If the lacquers are baked at about 180° C the coatings are also stable against corrosion by motor fuels.

Example 3

792 parts of a mixture consisting of hexanetriol and octanetetrol (obtained as a residue in the distillation of 1,3-butylene glycol formed by hydrogenation of commercial aldol) are heated for 5 hours together with 584 parts of adipic acid at about 240° C. A soft resin having an acid number of 10 is formed while 148 parts of water are separated.

120 parts of the said resin are dissolved in 160 parts of amyl alcohol. 40 parts of urea and 180 parts of 40 per cent formaldehyde are added and the whole is heated for 3 hours at 95° C while stirring. The volatile parts are distilled off until a residue of 310 parts is left. A resin is obtained which after dilution, for example with 70 parts of amyl alcohol, may be employed in the same manner as the resin obtainable according to Example 2.

Example 4

130 parts of glutaric acid are heated together with 300 parts of trimethylopropane for about 10 hours at 200° C. A soft resin of the acid number 1.5 is obtained.

Instead of glutaric acid the equimolecular proportion of adipic acid may be employed. Higher amounts of dicarboxylic acids, for example 300 parts of adipic acid, may also be employed instead, resins of higher acid number thus being obtained (in the case of 300 parts of adipic acid the acid number is about 28). By working in vacuo the reaction period may be considerably shortened.

A mixture of 735 parts of 30 per cent formaldehyde, 192 parts of urea, 25 parts of hexamethylene tetramine and 960 parts of normal butanol is heated for about 1 hour to boiling while reflux cooling. 400 parts of one of the resins obtainable according to paragraphs 1 and 2 are added and the whole is heated to boiling while distilling off water and butanol and recycling the latter until practically no water distills off. The product obtained is preferably diluted with normal butanol to form a 50 per cent solution.

75 parts of the said solution are mixed with 30 parts of alcohol and 8 parts of a 5 per cent solution of benzene sulfochloride in alcohol. The mixture thus obtained is brushed or sprayed onto wood. The lacquer is dry already after 2 hours and after 10 hours it is completely hardened. Without the addition of benzene sulfochloride it can be stored for any desired period. Without the said addition the lacquer may also be hardened by baking. The lacquer is compatible with pigments whether it contains the said hardening agent or not. It is also very suitable as a binding agent for abrasive papers fast to water and benzene.

100 parts of the resin disclosed above are mixed with a solution of the equal amount of the glutaric acid (or adipic acid) -trimethylopropane condensation product which has been employed for the preparation of the resin in 200 parts of butanol. After diluting the mixture with 25 parts of alcohol and 25 parts of toluene and adding 2 parts of a 1 per cent methyl-alcoholic hydrochloric acid solution a lacquer is obtained which (if desired after further dilution) may be sprayed on a thin natural silk fabric yielding an excellent oil-skin which is suitable for electrical isolating purposes and as a water-tight fabric. It is possible to apply several coatings of the said kind, each coating being allowed to

harden for a short period and if desired each coating being polished before applying the next one. Oil-skin thus obtained does not show the undesired property of becoming soft and sticky (syneresis) as is the case with oil-skin prepared by means of drying oils in consequence of a decomposition of the said oils; it is fast to light and stable to oils, fats and motor fuels.

The lacquer solution is suitable for example for impregnating pipes of flexible material or linen for tents. If about 10 per cent of titanium white are added to the lacquer and it is brushed onto fabrics excellent oil cloth and artificial leather can be obtained. Frequently it is advantageous for this purpose to prime the fabrics with an aqueous dispersion of polyvinyl compounds.

The lacquers are suitable also for the preparation of japanned leather. The lower layers of

the lacquer are preferably produced by means of relatively soft resins of the type in question. In view of the colorlessness of the binding agent it is suitable to produce even pure white japanned leather.

Example 5

538 parts of a 50 per cent normal butanol solution of a urea-formaldehyde condensation product produced in the presence of butanol are heated for 3½ hours at 135 to 140°C in a pressure-vessel together with 394 parts of a condensation product from trimethylolpropane and adipic acid produced according to Example 4. A solution is thus obtained which is excellently compatible with pigments and which dries with high gloss. The solution is suitable for producing lacquers to be baked.

WERNER WOLFF.

ALIEN PROPERTY CUSTODIAN

METHOD OF WORKING UP HIGH MOLECULAR POLYVINYL CHLORIDE

Herbert Berg, Julius Hiernels and Hans Machemer, Burghausen, Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 26, 1940

In the Patent Application S.N. 203 674 is described that mixtures of usual softeners, f.i. mixtures of tricresylphosphate and esters of high molecular fatty acids with univalent alcohols are well suited as softeners for high molecular polyvinyl chlorides manufactured according to the above named application.

There has been found by further working that mixtures of a special suitability are esters of polyhydric alcohols. Especially the esters of glycoles—one hydroxyl group of which being etherified if necessary—or dihydroxy ethers with acids of at least 4 preferably 6 or more carbon atoms are taken in consideration for this purpose. E.g. butandiol, ethoxy butyl alcohol, diethylene glycole, triethylene glycole, ethylene glycole monomethylether and ethylene glycole monoethyl ether may be called as glycole components of the esters to be applied according to the invention; acid components may be f.i. caproic acid, diethyl acetic acid, ethyl caproic acid, phenoxy acetic acid, dimethyl phenoxy acetic acid, chlorine phenoxy acetic acid and diglycolic acid. If the esters of dihydroxy ethers are employed the effect of the component according to the invention is so intensive that the applying of usual softening agents as f.i. tricresylphosphate may be omitted.

These softening agents resp. combinations of softeners in polyvinyl chloride yield composition of matter with an excellent heat stability and a resistance to cold not obtained until now. E.g. the esters of butandiol with phenoxy acetic acid, chlorine phenoxy acetic acid or with dimethyl

phenoxy acetic acid yield—f.i. in combination with tricresylphosphate—heat stabilities of 245, 240 resp. 210 minutes measured according to the usual stability test which consists in heating the substance in a current of nitrogen at 170° C and in determining the time passed until the first splitting off of hydrogen chloride is shown by a solution of silver nitrate. Also by esters of not carbocyclic acids heat stabilities can be obtained lying far above those obtained until now. E.g. a stability of 130 minutes is obtained—even without an addition of tricresylphosphate—by applying the esters of diethylene glycole and of 2-ethyl caproic acid.

By the above described softening agents extraordinary resistances to cold can also be obtained. E.g. the substances of polyvinyl chloride produced with diglycolic acid esters are useful down to -40°C. But also with diethylene glycole esters of caproic acid a similar high resistance to cold can be caused.

This surprising increase of the resistance to heat and cold obtained by the softening agents according to the invention is combined with an excellent effect also on the mechanical properties, as e. g. on the resistance to pressure and tearing, bending strength, resistance to notching, resistance to abrasion. They also have a favorable influence upon the working up of the composition of matter.

HERBERT BERG.
JULIUS HIERNEIS.
HANS MACHEMER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREPARATION OF ANHYDROUS COMPOUNDS OF THE PENTITES

Felix Grandel, Emmerich/Rhein, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed November 26, 1940

The preparation of anhydrous bodies of the hexites by way of distillation in the presence of catalysers is already known. Anhydrous compounds of the pentites, however, have not yet been prepared.

It has now been found that pentites can be transformed into anhydrous compounds, if the pentites are heated to higher temperatures, and/or are treated with catalysers promoting the splitting-off of water. Methionic acid is particularly well suited for use as catalyser.

In consequence of the reduction in size of the molecules due to the splitting-off of water the anhydrous compounds are distillable. In the process of preparing anhydrous pentites under the present invention the conditions of work are to be selected in such a way that a too extensive undesired splitting-off of water in the direction towards furfural is prevented.

The anhydrous pentites are capable to be readily esterified with acid. They can be advantageously used as esterifying agents in the fat and lacquer industries, as softening agents in the varnish industry, and for the manufacture of printing cylinders and oil cloth, in the motorcar industry as a material for the protection from low temperatures, as basic material for ointments in the pharmaceutical and cosmetic industries, etc.

Examples

1. 60 milligrams of methionic acid are admixed to 60 grams of xylite, whereupon the mixture is stirred for two hours at ordinary tempera-

ture, then heated up to 50 to 70 centigrades for one hour, and thereafter cooled down to room temperature, whereupon the water is distilled off, at first in vacuo, and later on at a still further reduced pressure (a high vacuum of 3 to 5 millimeters of Hg). The residue is passed through a high-vacuum distillation process, in the course of which, in addition to but a small quantity of fore-shot, the anhydrous compounds will come over at 218 centigrades and 8 millimeters of Hg as a fair and viscid oil.

2. 50 grams of xylite are heated up to 120 centigrades for one hour together with 2% of coal, subsequently filtered, when still hot, and quickly distilled off in vacuo at a 5 mm column. After fractionation one will obtain:

Mono-anhydrous xylite	KP 207° 5 mm Hg	34 g=68%
Di-anhydrous xylite	KP 170° 5 mm Hg	3 g=5%

Either of these compounds is a fair and viscid oil of yellowish shade.

3. 50 grams of xylite are quickly heated in vacuo up to 250 centigrades as a minimum together with 5% of Zn Cl₂. An oil mixture, light-brown in color, will pass over, from which after fractionation the following will be obtained:

Mono-anhydrous xylite	KP 207° 5 mm Hg	20 g=40%
Di-anhydrous xylite	KP 170° 5 mm Hg	10 g=20%

Other catalyzers, e.g. aluminum oxide, which do not display their effect in the gaseous phase, can also be used as catalyzing agents in the place of methionic acid, coal, chloride of zinc.

FELIX GRANDEL.

ALIEN PROPERTY CUSTODIAN

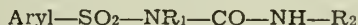
MAKING N-SULFONYLUREAS

Erich Haack, Radebeul, near Dresden, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed December 7, 1940

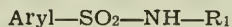
As a general rule urea derivatives of aromatic sulfonic acids which are substituted at the nitrogen cannot be prepared in the simple manner of a reaction of ureas upon sulfonylchlorides, as it is the case in obtaining the corresponding urea derivatives of the organic carboxylic acids. It is true that hydrogen chloride is split off during the reaction, if we attempt such a reaction between urea and sulfonylchloride; still we do not obtain the sulfonylurea, but merely sulfonic acids alongside of products derived from urea by splitting off water, or products of polymerisation thereof, such as dicyandiamide.

The desired N-sulfonylurea may be expressed by the formula:



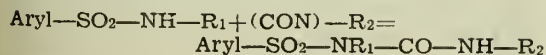
wherein aryl is an unsubstituted or substituted aromatic nucleus or condensed aromatic system, and R_1 and R_2 are hydrogen, alkyl, aralkyl or aryl radicals.

This invention is based upon the surprising discovery, that a product of said formula may be readily and easily obtained by starting from N-sulfonylamides of the formula:



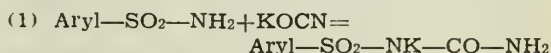
and by subjecting them to a treatment by the same methods which are commonly used for converting amides into ureas. The agents used in these methods are cyanic acid, isocyanic acid in the form of its esters, or compounds which change during the reaction into cyanic or isocyanic acid or from which these compounds are split off, e.g. nitrourea, urea, urethane and the like. Since the reaction is comparable to that of amines, it is more particularly rendered surprising by the acid character of the sulfamides on account of which salts of the cyanic acid or of the nitrourea may also be used, or basic compounds or acid binding salts like carbonate of soda may be present. In that case and provided also that a hydrogen atom is linked to the nitrogen atom neighbouring the sulfonyl group, the salts of the N-sulfonylureas, which react substantially neutral in watery solution, may be immediately obtained.

In the end there reactions take place according to the following formulae:

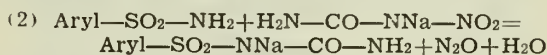


In case R_1 is hydrogen, and potassium cyanate

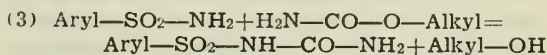
is the cyanic acid derivative used, the following course of reaction may be suggested:



For nitrourea-sodium:

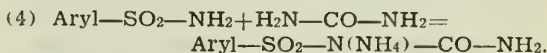


For urethane:

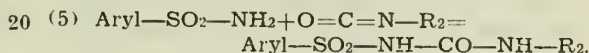


wherein alkyl stands for an alkyl-radical.

For urea:



For isocyanic acid ester:



Generally speaking the reaction is preferably carried out under heat, e.g. at temperatures between 60° - 100° C.

If the resulting N-sulfonylureas still carry hydrogen at the nitrogen atom which adjoins the sulfonyl group, they are strongly acid compounds which yield neutral alkali salts and are therefore most readily soluble in soda. If that is not the case, they are neutral compounds.

Compounds of this invention may be used for technical as well as medicinal purposes. Of particular value are compounds, which have an amino group in p-position to the SO_2 -group on the aromatic sulfonyl nucleus and also carry a hydrogen atom on the nitrogen atom which is linked to the sulfonyl radical. These compounds serve as remedies for infectious diseases. The amino group may either be present as such, as illustrated by example 7, or it may be introduced as an acylated group together with the sulfonic acid component (examples 3 to 6) to be subsequently made free by saponification, or as a nitro-group, which is reduced to an amino group after the urea compound has been prepared.

Example 1

50 gr of benzenesulfamide and 28 gr of potassium cyanate are boiled in alcohol (80-90%), until a test shows complete solubility in water. That means that the potassium salt of the benzenesulfonylurea has been formed, which may be recrystallized as such from water, possibly under addition of potassium carbonate in order to reduce the solubility. When dissolved in water

and acidulated by glacial acetic acid, the free benzenesulfonylurea is presipitated with a yield of about 90% and shows, when dry, a melting point of 170–171° C.

Example 2

50 gr of p-toluenesulfamide and 25 gr of nitro-urea-sodium are gently heated in alcohol (80–90%) until the evolution of nitrous oxide is completed. The alcohol is distilled off and the residue is placed into a liberal amount of water, neutralized by carbonate of soda and filtered under suction off the starting material which has remained undissolved. A yield of approximately 80% of p-toluene-sulfonyl-N-urea crystallizes out of the filtrate after acidulation. The rest may be recovered as starting material from the portion which is not soluble in alkaline solution. By increasing the quantity of nitro-urea the yield may be substantially improved. Purification of the toluenesulfonyl-urea is preferably brought about by crystallization of the potassium salt from a small quantity of water to which potassium carbonate is added. The beautiful crystals may be dissolved in water and the free urea may be precipitated from the solution by acetic acid. It decomposes when melted at 184°–188° C.

Example 3

50 gr of acetylsulfanilamide and 30 gr of Potassiumcyanate are heated several hours in 200 cc of alcohol and 20 cc of water. Upon cooling the reaction product is sucked off and weighs 70–71 gr, after drying. This represents a substantially 100% yield of the potassium salt of the p-acetylsulfanilylurea. The salt crystallizes out of water under addition of potassium carbonate in the form of beautiful, long needles. By precipitation with acetic acid the free acetylsulfanilylurea may be obtained, which decomposes at a melting point of 185°–188° C.

Example 4

A similarly satisfactory yield of acetylsulfanilyl-urea may be obtained, if 50 gr of acetylsulfanilamide, 50 gr of nitro-urea and 30 gr of carbonate of soda are heated to the boiling point in 80% alcohol for 5–6 hours. After the alcohol has been boiled off, the mass is almost completely soluble in water and represents the sodium salt of the desired urea.

Example 5

	Parts
Acetylsulfanilamide -----	5
Urea -----	3
Carbonate of soda -----	2
Alcohol -----	15
Water -----	5

are heated on a steam bath. Soon the sublimation of ammonium carbonate or—carbamate sets in, and after about 10–12 hours the reaction is approximately half complete, as recognized from the portion which has been rendered water-soluble. Further heating fully completes the reaction. A solvent of a higher boiling point, like butylalcohol, may also be used, as well as other basic compounds, such as potassium hydroxide, potassium carbonate, sodium alcoholate, or a tertiary amine, the reaction thus being in some instances materially accelerated.

Similar results are obtained with urethanes, e. g. ethylurethane, the reaction being however slower than in the case of urea.

In all these cases, the acetylsulfanilylurea is

obtained which decomposes after melting at 185°–188° C. When saponified with caustic soda solution or concentrated hydrochloric acid it yields the p-aminobenzene-sulfonyl-N-urea which decomposes at its melting point of 149°–154° C.

Example 6

20 gr of acetylsulfanilamide and 12 gr of phenylisocyanate are heated for an extended period of time to 100° C. The product of reaction is washed up in water, neutralized, while hot, by a sodium carbonate solution and, after cooling, sucked off from the insoluble sediment. Acetic acid precipitates from the filtrate a thick white deposit of the free urea derivative, which is preferably crystallized by way of the potassium salt from water with addition of sodium carbonate. The potassium salt forms beautiful needles, and from these we may obtain by means of acetic acid a good yield of the N-(acetylsulfanilyl)-N'-phenylurea.

Example 7

p-Aminobenzenesulfonylcarbamide is produced as follows:

350 gr of sulfanilamide, 178 gr of potassiumcyanate (technical) and 1050 cc of denatured alcohol are boiled for 6 hours under reflux. As soon as the original mass has passed into solution, the potassium salt of the new compound starts crystallizing out until it finally forms a thick mass of crystals. The mass is sucked off while hot and again washed with the first named amount of hot 90% alcohol. Upon drying 470 gr of crystal powder are obtained. These are stirred up with 550 cc of cold water, and washed with 50 cc of a saturated potassium carbonate solution. About 450 gr of the potassium salt of the p-aminobenzenesulfonylcarbamide are obtained, i.e. 87% of the theoretical yield. The missing part is contained in the mother liquor in form of sulfanilamide and further heating with potassium cyanate will convert that part also to potassiumaminosulfonylcarbamide. The potassium salt crystallizes from water in colorless flakes, which exhibit but moderate solubility in cold water, particularly so, when potassium salts or alcohol are added. Upon dissolution in four times the amount of hot water and addition of acetic acid, the free sulfonylcarbamide is precipitated in large needles, which contain 1 mol of crystal water.

The sodium salt is readily soluble in water and completely neutral in reaction. When boiled for some time in neutral, acid or alkaline solution, the compound is hydrolized into sulfanilamide. The free acid, which contains crystal water, decomposes under effervescence at about 125°–127° C.

Other isocyanic acid esters add in like manner, or even still more readily, to sulfamides to form N'-substituted N-sulfonylureas.

Having thus given a careful outline of my invention in detail, yet I do not wish it to be limited thereby, except as the state of the art and the appended claims may require, for it is obvious that various modifications and changes may be made in the form of embodiment of my invention, without departing from the spirit and scope thereof.

Some of the subject matter herein described is dealt with or claimed in my companion patent application, Serial No. 369,117, filed December 7th 1940, for N-sulfonylureas and method of making same.

ERICH HAACK.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR MANUFACTURING LITMUS DYESTUFF

Haruyo Asahina, Kawaraki-Mura, Japan; vested
in the Alien Property Custodian

No Drawing. Application filed December 12, 1940

This invention relates to improvements in the manufacture of litmus dyestuff by treating β -orcin with ammonia in the presence of an alkali.

Litmus dyestuff is generally prepared by fermentating in the open air *Rocella tinctoria* D.C., a kind of lichen or its analogous vegetable such as *Rocella Montagnei* Bel. *R. fuciformis* D.C., *R. fucoides* Wain and *Ochrolechia tartarea* Massal, with an ammonium salt added thereto under an alkaline condition.

It requires as long time as about 40 days to produce litmus dyestuff by this known method, and the lichen, the raw material, is found only in very limited parts of the world. These are inevitable drawbacks of the known process.

According to this invention an easily obtainable material, β -orcin or its derivatives as diffractaic acid which is easily decomposed and produces β -orcin is employed as the raw material, and litmus dyestuff or analogous one can be produced in a very short time.

The new process consists of treating the raw material abovementioned with ammonia or an ammonia producing substance in the presence of an alkali, e. g. carbonate of alkali, bicarbonate of alkali, and caustic alkali.

This process is very simple and requires only a few hours for producing litmus dyestuff, and the sensitiveness of the product is not inferior to the best litmus dyestuff now sold in the markets.

A kind of lichen such as *Usnea diffracta* Wain which is quite different one from the aforementioned *Rocella* and *Ochrolechia*, contains a de-

rivative of β -orcin and is available as the raw material for this invention.

The process is described by way of following examples.

5 Example 1. 5 parts of β -orcin, 120 parts of sodium carbonate, 50 parts of ammonia and 50 parts of water, all in weight, are mixed together, and this mixture is heated for a few hours at a temperature between 60°C to 80°C when blue litmus
10 dyestuff is produced.

Example 2. 5 parts of β -orcin, 15 parts of caustic potash, 5 parts of ammonium carbonate and 30 parts of water, in weight, are mixed together, and this mixture is heated for a few hours at a temperature between 50°C to 80°C.
15

Example 3. 10 parts of diffractaic acid, 10 parts of caustic soda and 100 parts of water are mixed, and this mixture is heated for a few hours, thereafter 25 parts of 30% ammonia water is added to the mixture to react at a temperature between 50°C to 80°C.
20

Example 4. 200 parts of *Usnea diffracta* Wain, 10 parts of caustic soda and 200 parts of water are mixed, and this mixture is heated for a few hours, thereafter 50 parts of 30% ammonia water is added to the mixture to react at a temperature between 50°C to 80°C.
25

In these examples the reaction can be accomplished without heating, but in that case it requires a long time till the product is obtained.
30

HARUYO ASAHINA.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF SYNTHETIC RUBBER

Carl Zerbe, Hamburg, Johannes Jaenicke and
Otto Schweitzer, Frankfurt A. M., Germany;
vested in the Alien Property Custodian

No Drawing. Application filed December 23, 1940

This invention relates to a process of producing synthetic rubber.

For quite some time, products resembling natural rubber as to properties and applicability have been prepared from monomeric butadiene hydrocarbons and their derivatives. Of these substances the mixed polymerization product of butadiene and styrene or acrylonitrile has given particular satisfaction during the last years, though these substances differ from natural rubber not only in the properties due to the chemical difference of their fundamental substances but also in the usually considerable cyclization of the molecules forming during polymerization and being per se already high-molecular. During subsequent working both causes bring about a behavior of these polymerization products which differs from that of natural rubber. The masses are comparatively hard, so that it is difficult, with the usual mixing arrangements, to prepare therefrom homogeneous mixtures with the usual additions, as fillers and vulcanizing agents. The finished mixtures are, as a rule, stiff and can be molded only with difficulty.

To facilitate the working of these products it was necessary to resort to measures, including for instance different decomposition methods, absolutely unusual in working natural rubber. The use of softeners and similar expedients, known already from the working of natural rubber, has been accepted to an increasing extent also in working the new polymerization and mixed polymerization products. A number of aids specifically effective in working these products was discovered also. Special mention in this respect deserve hydrocarbon mixtures partly unsaturated and partly soluble in concentrated sulfuric acid, reactive and possibly distilled at reduced or atmospheric pressure, which accrue, when all sorts of mineral oil fractions are refined with selective solvents or which are obtainable from the acid resins developed during refining of the oils with concentrated sulfuric acid by neutralization or hydrolysis or extraction or, possibly, distillation. These substances are added during production of synthetic rubber mixtures in the mixing arrangements at an extraordinarily great expenditure of energy at the beginning of this procedure when these substances are not yet distributed in the polymerization product.

It has now been found, according to the invention, that these substances obtained in refining mineral oils may be added in dissolved or dispersed form to the substances to be polymerized either prior to the beginning or at least the completion of the polymerization and that the additions are then ideally distributed among the macromolecules forming during polymerization. The hydrocarbon mixtures referred to above are thus added to the monomeric compounds or mixtures thereof serving for forming

the polymerization products, and this should be done at an early stage of polymerization at the very latest. The amounts of the additions may be adapted within wide limits to the requisite reaction conditions and the expected properties of the final product. It might easily happen in this connection that, apart from mere physical intercalation, the reactive portions of the additions according to the invention are more or less chemically combined with the macromolecules forming, possibly through residual affinities. A particularly favorable distribution is further insured by the fact that the low-molecular portions may serve as solvents for the hydrocarbon mixtures according to the invention.

The process may be applied to the production of the polymerization products of butadiene, its homologues and derivatives, or of the mixed polymerization products thereof with vinyl compounds, as styrene or acrylonitrile, or of the polymerization products of other monomeric ethylene and vinyl compounds. The homologues of butadiene include also methyl-butadiene, or isoprene, which supplies the true synthetic rubber.

To attain the effects contemplated by the invention the extracts or distillates obtainable by refining mineral oils with selective solvents like furfurole sulfur dioxide, sulfur dioxide in mixture with organic solvents like benzene, etc., or from the acid tars produced by refining the oils with concentrated sulfuric acid after neutralization with suitable agents, or by hydrolysis with water, water vapor, etc., may be employed. These substances represent mixtures of hydrocarbons partly unsaturated and partly soluble in concentrated sulfuric acid. Furthermore, certain mineral oils occurring in nature, such as the miri oils, which are rich in substances showing a tendency to resinify, are also adapted for the process.

A particular advantage afforded by the process is that the softening additions are ideally distributed already in the synthetic rubber before the latter is worked on the rollers. The mixture of substances thus produced is therefore plastic enough for the first stage in the rolling operation. It is further highly advantageous that the heat liberated during polymerization is absorbed also by the substances added according to the invention. Owing to the loosening up of the arrangement of the particles to be polymerized, a welcome damping of the frequently quite stormy course of the reaction is effected.

The mixtures may be polymerized undiluted or in the presence of solvents or in emulsion. Depending on the process applied, the usual catalysts, as metallic sodium, tin tetrachloride, peroxides, etc. may be used.

CARL ZERBE,
JOHANNES JAENICKE,
OTTO SCHWEITZER,

ALIEN PROPERTY CUSTODIAN

PROCESS OF IMPROVING SYNTHETIC RUBBER AND FACILITATING THE WORKING THEREOF

Carl Zerbe, Hamburg, Johannes Jaenicke and Otto Schweitzer, Frankfurt A. M., Germany; vested in the Alien Property Custodian

No Drawing. Application filed December 23, 1940

This invention relates to a process of improving synthetic rubber and facilitating the working thereof.

The kinds of rubber obtainable by synthesis are produced as a rule by emulsifying in water the monomeric substances to be polymerized or mixtures thereof while adding the usual emulsifying agents and catalysts, and then polymerizing them. The synthetic rubber latex thus produced resembles in many respects natural rubber, is like the latter made into sheets by coagulation, washing, drying and rolling and constitutes in this form, as smoked sheet or crepe rubber, a raw material for the industry concerned.

These synthetic substances differ, however, from natural rubber not only in their properties due to the chemical difference of their fundamental substances but also as to the usually considerable cyclization of the molecules forming during polymerization and being per se already high-molecular. Due to the difference existing between the chemical composition of their parent substances and that of natural rubber and simultaneous heavy netting through cyclization, these synthetic products show of course a different behavior than the natural product practically at every stage of subsequent working. Particularly when crude mixtures are prepared on the mixers and subsequently molded, synthetic products are extraordinarily hard and require therefore a greater expenditure of energy for these operations than natural rubber. The uniformity of the mixtures found in natural rubber, that is, the good distribution of the ingredients, is also attainable only with difficulty in synthetic products. The measures hitherto proposed to overcome these troubles, such as thermal or chemical decomposition, improve matters to some extent but fail to insure satisfactory working. The addition of softeners of different kinds gives only partial relief, apart from the fact that these softening substances can be added only in slight quantities. Softeners of this class are added during production of the compounds in the mixing arrangements, which still requires extraordinarily great amounts of energy at the beginning of this step when the substances have not yet been distributed in the polymerization product.

As aids in working synthetic rubber, the extraction residues accruing in the refining of different mineral oil fractions with selective solvents, the distillates thereof and also the corresponding hydrocarbon mixtures, partly unsaturated

and partly soluble in concentrated sulfuric acid, obtainable from the acid tars developed during refining of crude oils with concentrated sulfuric acid by neutralization or hydrolysis or extraction and, possibly, distillation have given particular satisfaction. Suitable for this purpose are also the natural unchanged crude oils, as miri oils and similar hydrocarbon mixtures, which are especially rich in substances tending to resinify.

It has also been proposed to add these substances to the latices of the various sorts of synthetic rubber so as to provide a denser structure for the objects directly produced from latex under the usual processes.

It has now been found, according to the invention, that by the joint coagulation of mixtures of synthetic rubber latices, or of dispersions of synthetic rubber derivatives, and of the emulsions of softening substances and by washing, drying and rolling products are obtained that are adapted to a particularly high degree to serve as starting materials for the rubber industry. Such joint coagula representing intermediate products may be produced for instance by making use of the possibly previously concentrated aqueous dispersions of the polymerization products of butadiene, its homologues and derivatives, or of the mixed polymerization products thereof with vinyl compounds, as styrene or acrylonitrile, of similar ethylene and vinyl compounds and also of the conversion products of aliphatic dihalogen compounds and alkali polysulfides. The polymerization products of methyl-butadiene, or isoprene, which must be considered a homologue of butadiene, are accordingly also included in this class.

In further accordance with the invention, the additional substances to be used comprise the extracts or distillates obtainable by refining mineral oils with selective solvents, as furfurole, sulfur dioxide, sulfur dioxide in mixture with organic solvents like benzene, etc., or from the acid tars produced in refining with concentrated sulfuric acid either after neutralization with suitable agents or by hydrolysis with water, water vapor, etc. These substances represent mixtures of hydrocarbons partly unsaturated and partly soluble in concentrated sulfuric acid. Suitable for the process are also certain crude oils occurring in nature, such as miri oils, which are rich in substances tending to resinify.

The common coagula can be prepared also by adding the softening agents to the basic materials of synthetic rubber already during produc-

tion, that is, before the completion of polymerization at the earliest, whereupon these mixtures are completely polymerized, coagulated and subsequently worked as usual. A substance may therefore be added in the form of aqueous dispersions or emulsified already in the emulsion of the polymerization products, in other words, it may be added at any time between actual polymerization and the production of the coagula. The quantities of the additional substances according to the invention may vary within wide limits.

The application of the process according to the invention insures such fine distribution of the softening additions in synthetic rubber that

working of the latter on the mixers is surprisingly facilitated even at the beginning of the mixing operation. If softening to a particularly high degree is desired, the mixtures of substances thus produced may be decomposed by known methods prior to being treated in the mixing arrangements. It is even possible to subject the mixtures when still in latex form to a heat or chemical treatment, for instance with the aid of oxidizing agents, and then to continue further working of the mixtures formed.

CARL ZERBE.
JOHANNES JAENICKE.
OTTO SCHWEITZER.

ALIEN PROPERTY CUSTODIAN

FIBROUS MATERIALS

Heinrich Ulrich, Ernst Ploetz, and Eberhard Nold,
Ludwigshafen-on-Rhine, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed December 31, 1940

The present invention relates to media for the improvement of fibrous materials.

We have found that dispersions containing besides paraffin waxes or substances of similar physical nature and water polymerized alkylene imines or conversion products thereof, are highly efficient media for the improvement of fibrous materials, such as textiles, leather or paper. The dispersions may be made in any desired manner with or without the application of dispersing agents and/or protective colloids.

As suitable polymerized alkylene-imine substances we mention, for example, the polymerization products of ethylene-imine, 1,2-propylene-imine, 1,3-propylene-imine, 1,2-butylen-imine, N-methylethylene-imine, N-cyclohexylethylene-imine or phenylethylene-imine. As paraffin waxes or substances of similar physical nature we may mention hard paraffin wax, soft paraffin wax, chlorinated paraffin waxes, paraffin oil, carnauba wax, Japan wax, montan wax, stearic acid, the esters, anhydrides or amides thereof, octodecylamine, octodecyl alcohol, dodecylcyclohexanol, montanyl alcohol, tallow, sperm-aceti oil, ketones from high-molecular fatty acids and the alcohols and hydrocarbons obtainable from these ketones by reduction, furthermore octodecylpolyvinyl ether, isobutylpolyvinyl ether and the like. Mixtures from several of the aforesaid substances are also suitable for the purposes of the present invention.

In preparing the emulsions we may employ as dispersing agents, for example, soaps, water-soluble salts of alkylnaphthalenesulphonic acids or of sulphonation products from olefines or higher-molecular alcohols, furthermore polyglycol ethers from fatty alcohols or high molecular aliphatic amines, or fatty acid polyglycol esters. As protective colloids may be used, for example, glue, gelatine, agar-agar or dextrine.

In preparing the dispersions it is preferable to employ the paraffin wax or the substance of similar physical nature in preponderance to the polymerized alkylene-imine. Thus, for example, the dispersions may contain from about 20 to 30 per cent of paraffin and from 1 to 10 per cent, advantageously only about 1 to 5 per cent, of polymerized alkylene-imine. Besides the said constituents, the dispersions may yet contain other constituents, such as are compatible with the constituents already present, as for example dye-stuffs, plasticizers, inorganic salts, zinc oxide, titanium dioxide, zirconium oxide, aluminum hydroxide, urea or starch.

The treatment of the fibrous materials, for ex-

ample textiles, may be performed by employing baths in which the said dispersions have been incorporated. The materials so treated are then dried and, if desired, subsequently heated for a longer time, for example at about 80 to 100°C. While treating the materials with the dispersions or while subjecting the so treated materials to the subsequent drying and heating treatment, it is often of advantage to treat them simultaneously with aldehydes, such as formaldehyde, paraformaldehyde or acetaldehyde.

By treating textiles, such as cotton, wool or artificial silk fabrics, papers or leather with the dispersions according to the present invention, an excellent and long-lasting water-repellant effect is imparted to them. According to the substances contained in the dispersions in addition to the alkylene-imine, the fibrous materials simultaneously are imparted an excellent softness or fullness and/or surface smoothness. They may also get an increased affinity to acid dye-stuffs and/or a diminished absorptiveness to water. When applied to paper, the treatment with the dispersions especially effects a good fastness to moisture as well as to rubbing in a wet state.

The following Examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said Examples. The parts are by weight.

Example 1

100 parts of polymerized ethylene-imine are dissolved in 700 parts of water at 70°C, whereupon a mixture of 392 parts of soft paraffin wax and 168 parts of paraffin oil, having been heated to about 100°C, is finely distributed in the said solution by means of a dispersing machine. The emulsion is then diluted with 640 parts of water at a temperature of 70°C and then passed through a homogenizing machine for some minutes under a pressure of 120 atmospheres. The finished emulsion is allowed to cool.

A viscose artificial silk fabric is soaked in a bath to each liter of which the dispersion so obtained has been added in an amount of 10 to 100 grams, and then dried on a drum at from 100 to 110°C. By this treatment the fabric is made markedly water-repelling, its perviousness to air being unimpaired.

Example 2

70 parts of polymerized ethylene-imine are dissolved in 220 parts of water at a temperature of 70°C and then a mixture of 220 parts of hard

paraffin wax and 11 parts of colophony, fused at about 100°C, is distributed in the solution so obtained by means of a dispersing machine. The emulsion is then diluted with another 200 parts of water, pumped through a homogenizing machine for some minutes under a pressure of 70 to 80 atmospheres and afterwards united with a mixture of 200 parts of a solution of an aluminum oxide gel, 60 parts of formic acid and 39 parts of water. The emulsion obtained is then allowed to cool.

Example 3

250 parts of a hydroxyethylated stearic acid monoethanol amide are intimately mixed with 750 parts of an aqueous solution containing 50 parts of polymerized ethyleneimine under vigorous agitation until a homogeneous emulsion re-

sults. Fabrics of cell-wool treated with solutions containing from 2 to 4 per cent of the emulsion so obtained are imparted a soft and smooth touch which remains unaffected by washing.

Example 4

250 parts of octodecyl alcohol are melted and mixed with a 13 per cent solution of polymerized ethylene imine in a turbo mixer. The dispersion so obtained is stable and may be easily diluted. Fabrics treated with the diluted dispersion are imparted a soft touch and water-repelling properties.

HEINRICH ULRICH
ERNST PLOETZ.
EBERHARD NOLD.

ALIEN PROPERTY CUSTODIAN

RESINOUS CONDENSATION PRODUCTS

Wilhelm Fitzky, Frankfurt am Main, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed January 3, 1941

The present invention relates to resinous condensation products.

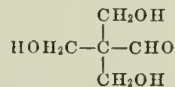
I have found that new synthetic resins are obtained by condensation of saturated aliphatic aldehydes and ketones containing at least two $\text{—CH}_2\text{OH}$ groups at the carbon atom adjacent to the carbonyl group with monobasic or polybasic carboxylic acids. In most cases it is possible to work without condensing agents; catalysts of strong action such as mineral acids are even detrimental. In some cases organic acids of medium strength or the anhydrides thereof may have a favorable influence on the condensation, such as for instance phthalic anhydride, which may also take part in the reaction. As the methylol compounds of aldehydes are starting materials which are readily accessible on an industrial scale (cf. my co-pending U. S. patent application Ser. No. 263,408, filed March 22, 1939), the condensation products are of special importance. The substances obtained show no properties owned by aldehydes or ketones; the free carbonyl group disappears during the condensation, presumably owing to acetalization. This fact probably contributes to the formation of high molecular products suitable as plastic masses.

It is remarkable that one mol of hydroxymethylated aldehyde or ketone esterifies at most with one mol of a monobasic acid with formation of a product with a low acid number. If the one or other component is used in excess, this excess may be distilled off during the reaction or it may be removed unchanged from the mixture after the reaction. When using di-carboxylic acids one carboxyl group remains free. It is not possible to condense this carboxyl group with a further aldehyde or ketone; it may only be condensed with readily esterifiable components, for instance with mono-alcohols or amines, the catalytic action of mineral acid being necessary in the first-named case.

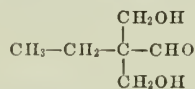
For the condensation there may be used any carboxylic acids of aliphatic or aromatic nature of lower or higher molecular weight, such as for instance acetic acid, propionic acid, butyric acid, caproic acid, heptylic acid, adipic acid, pimelic acid, maleic acid, benzoic acid, phthalic acid, abietic acid, (also in the form of the colophony), furthermore fatty acids from the first runnings obtained in the distillation of paraffin-oxidation products as well as the saturated carboxylic acids obtainable by oxidation of primary saturated aliphatic alcohols in the heat with caustic alkalies or hydroxides of alkali earth metals. As such primary alcohols there may, for instance, be

named the oily alcohol mixtures obtainable in the hydrogenation of carbon monoxide with application of pressure. The acids obtainable from these mixtures in the afore-mentioned oxidation essentially consist of aliphatic saturated acids of the constitution $\text{C}_5\text{H}_{10}\text{O}_2$ to $\text{C}_8\text{H}_{16}\text{O}_2$, they are presumably branched in neighbouring position to the carboxyl group. For the condensation there are further useful the anhydrides of all the above-named carboxylic acids, especially those of the dicarboxylic acids.

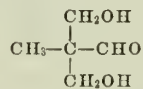
As the other component there may be used for instance: trimethylol acetaldehyde of the formula:



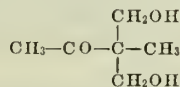
dimethylol butyraldehyde of the formula:



dimethylol propionaldehyde of the formula:



as well as the aldehyde containing hydroxymethyl groups which is obtainable from acetaldehyde and formaldehyde. All these compounds may be prepared according to the statements in my co-pending U. S. application Serial No. 263,408, filed March 22, 1939. The ketones containing $\text{—CH}_2\text{OH}$ groups which are obtainable according to the same process are not so highly important, for instance:



The condensation is suitably carried through at temperatures between about 100°C to about 200°C . In order to promote the removal of the water formed agents may be added which form with it azeotropically distilling mixtures, for instance toluene or xylene. Furthermore solvents such as butanol may be present.

According to the composition and the degree of condensation the resinous products are obtained in different states ranging from viscous oils to nonpliable or elastic resin. Their solubilities and their properties are of great variety as could be expected. The products are not only important in the field of plastic masses, but they are in part

also useful as textile adjuvants. They are especially suitable as starting materials for varnishes, lacquers and coatings.

The following examples serve to illustrate the invention but they are not intended to limit it thereto:

(1.) 120 grams of trimethylolacetaldehyde are slowly heated to boiling together with 300 grams of glacial acetic acid and 200 grams of toluene. The water which has been formed is distilled off with the toluene and separated therefrom. Thereafter the toluene is returned and distilled off several times until water passes over no longer. Finally the resin formed is freed under reduced pressure from all volatile constituents. For final purification it is treated with sodium carbonate solution and water and dried. 155 grams of a yellowish soft resin having the acid number 6 and the ester number 452 are obtained.

(2.) 110 grams of trimethylolacetaldehyde are heated within 30 hours to 180°C together with 150 grams of colophony WW and 200 ccm of xylene. In order to remove the excess of colophony, the solid resin is treated with ether. A light-yellow powder having the acid number 35 is obtained.

(3.) 344 grams of a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products with essentially unbranched length of chain of 6 to 9 carbon atoms are heated to 150°C with 240 grams of trimethylolacetaldehyde whereby homogenization occurs and the condensation is started. For finishing it, the temperature is then raised to 180°C (8 hours). In order to deacidify the product it is treated with sodium carbonate solution and then with water and dried. 410 grams of a yellowish, thick, resinous oil of the acid number 1.2 are obtained. From the sodium carbonate solution there are precipitated by means of acid 60 grams of an acid product containing a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products, which product may be used again.

(4.) 356 grams of a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products (according to Example 3) with an average molecular weight of 130 are mixed with 450 grams of an aqueous solution of trimethylolacetaldehyde of 80 per cent strength in which 30 grams of phthalic anhydride were previously dissolved in the heat and the water is distilled under reduced pressure. In order to effect the condensation, the temperature is raised first to a value above 100°C and then slowly under reduced pressure within 30 hours up to 180°C until water is no longer formed. The mixture is then dissolved in benzene, freed from acid with sodium carbonate solution and dried. A honey-yellow soft resin of the acid number 13 is obtained which is soluble in aromatic and aliphatic solvents. Instead of phthalic acid maleic acid may also be used for the condensation.

(5.) 274 grams of a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products are slowly heated under reduced pressure with 264 grams of dimethylolbutyraldehyde to 180°C. A resin is obtained which

is nearly equal to the product obtained according to example 3, but has a somewhat softer consistency.

(6.) 60 grams of trimethylolacetaldehyde are heated for 6 hours to 130°C together with 50 grams of phthalic anhydride. In order to remove the excess of phthalic acid the mixture is treated with benzene. The remaining glassy-brownish resin has an acid number of 203 and a saponification number of 413. It dissolves in cold caustic soda solution without saponification.

(7.) From a mixture of 75 grams of adipic acid and 120 grams of a solution of trimethylolacetaldehyde of 50 per cent strength the water is slowly evaporated within 15 hours and then heated for 2 hours to 160°C to 180°C. The originally turbid mass frothes, clears up and becomes more viscous. 90 grams of a resin are obtained which is insoluble in organic solvents, after cooling has a viscous elastic consistency, dissolves in cold dilute caustic soda solution, is precipitated again by means of an acid but saponifies by a prolonged heating with caustic soda solution and may then no longer be precipitated by means of an acid.

(8.) 150 grams of adipic acid are heated under a pressure of 100 to 200 mm with 320 grams of trimethylolacetaldehyde and 300 grams of a mixture of butanol and xylene for 18 hours to 120°C and the water is azeotropically distilled off. The resin is then treated with warm water for removing the adipic acid in excess and dissolved in butanol. 570 grams of a solution of butanol of the acid number 51 are obtained. This solution is heated with 136 grams of octadecylamine for 4 hours to 100°C. By evaporation a brown semi-soft product is obtained which has valuable textile-chemical properties.

(9.) 100 grams of a soluble condensation product from equimolecular quantities of maleic acid and trimethylolacetaldehyde (condensed at 100°C) of the acid number 201 and of the saponification number 436 are heated together with 200 grams of butanol, 100 grams of formaldehyde of 30 per cent strength, 80 grams of cetyl alcohol and 10 ccm of concentrated hydrochloric acid for 20 hours to 80°C, the aqueous part is then eliminated and the resin is heated for 10 hours at 130°C. After removal of a small excess of cetyl alcohol 155 grams of a thick oil of the acid number 10 is obtained.

(10.) 50 grams of phthalic anhydride are dissolved at 100°C in a solution of 600 grams of trimethylolacetaldehyde in 400 grams of water and then 580 grams of 2,4-dimethyl pentanic acid-1 (isoheptylic acid) are added and the water is slowly distilled off while stirring under reduced pressure. The temperature gradually rises to 180°C. When the evolution of water vapor and consequently the condensation is finished the mixture is freed from acid by treatment with dilute caustic soda solution and then washed with water and dried. A brownish, slightly sticky resin, soluble in aromatic solvents is obtained.

WILHELM FITZKY.

ALIEN PROPERTY CUSTODIAN

RESINOUS CONDENSATION PRODUCTS AND PROCESS OF MAKING THEM

Herbert Hönel, Vienna, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed January 3, 1941

This invention relates to the production of resinous condensation products from urea, formaldehyde and alcoholic compounds.

One object of my invention consists in producing modified urea resins in a more simple and economical way than heretofore known. Another object consists in producing modified urea resins which are novel per se. Further objects will appear hereinafter.

It is known that the condensation of urea with formaldehyde may be carried out in the presence of alcoholic solvents and in absence of water. The resin or resin solution obtained is particularly suited as a base for varnishes. Instead of urea and formaldehyde also dimethylolurea may be employed. The alcoholic compounds more or less take part in the reaction which is considered as an etherification with a part of the methylol groups. It is however inconvenient to use gaseous formaldehyde and on the other hand anhydrous polymers of formaldehyde as well as the isolation of dimethylolurea are expensive. Consequently it has already been proposed to avoid the isolation of dimethylolurea and only for a short time to react 1 mol of urea with about 2 mols of aqueous formaldehyde in the presence of an alkaline catalyst and a suitable alcoholic substance such as butanol and then to subject the reaction mixture to distillation. The distillate forms two layers, and the layer rich in butanol is continuously reintroduced into the reaction mixture, this procedure being continued, later on in the presence of acid catalysts, until the whole water is removed.

In all these processes only alcoholic solvents may be used which are compatible with water either already in the cold or at least at boiling temperature; such as is the case with the lowest members of alcohols including butyl alcohol or partial ethers or esters of ethylene glycol e. g. "Cellosolve". Butyl alcohol has an exceptional position because it is soluble in the reaction mixture in the heat and to a great part separates from the distillate in the cold. The portion remaining in the watery layer of the distillate, however, may only be recovered by troublesome and circumstantial fractionation. Still higher alcohols which practically would completely separate from the water in the distillate, fail in this process because they can not be combined with the reaction products from urea and formaldehyde mentioned above.

I have now found that sirupy condensation products practically completely free from water may be obtained in a simple way from aqueous

formaldehyde and urea, which products extraordinarily readily can directly be combined with alcoholic substances even such as are practically immiscible with water and fail in the processes described hereinbefore. These obviously very low molecular resinous condensation products which are readily soluble both in water and alcohol, are formed if 1 mol of urea is reacted with a quantity of formaldehyde considerably exceeding 2 mols, i. e. with about $2\frac{1}{2}$ –4 mols or more, in an alkaline, neutral or only slightly acidic medium during several hours at temperatures between 60 and 100° C. The range of hydrogen ion concentration suitable for the reaction corresponds to a pH of about 5.0–10.0. When subjecting the reaction mixture to distillation, suitably under diminished pressure at temperatures not exceeding 100° C, it will be found surprisingly that almost all the formaldehyde employed has entered the reaction (about 90% or eventually even 97%). Only if a considerable excess over four mols of formaldehyde had been employed the excess will appear in the distillate. The yield of the viscous, clear residue, after carefully being treated in vacuo, nearly exactly corresponds to the sum of the weights of the urea and of the formaldehyde (CH_2O) which did not distill off. From these facts I conclude that the condensation products obtained according to my process consist of trimethylolurea and tetramethylolurea respectively or occasionally of mixtures thereof with dimethylolurea, depending upon the proportions used and length of condensation etc.

Particularly when 3 or more mols of formaldehyde have been bound in my process, the condensation products obtained are readily chemically combined with long chain alcohols such as butyl alcohol or even higher ones, probably due to their solubility characteristics, as they are readily soluble in the lower alcohols to any proportion.

A process is known in which formaldehyde is used in excessive proportion corresponding to even almost $4\frac{1}{2}$ molecules per each molecule of urea. In this process, however, the condensation is strongly influenced by the considerable acidity of aqueous formaldehyde which generally shows a pH of 3–4 due to presence of formic acid. This acidity transforms the condensation product primarily formed to relatively high molecular stages and, when driving off the water, gelatinisation occurs even when still large proportions of water are present. Products obtained according to this known process fail in the combination with alcohols aimed at in my present process.

When combining the condensation products primarily achieved in my process as described above, with alcohols I generally add a suitable acidic substance in order to bring about a pH of the reaction mixture between about 5 and 6. If only the lowest members of alcohols or ethylene glycol ethers are used as modifying agents many inorganic or organic acids or acidic salts are serviceable, e. g. hydrochloric acid, phosphoric acid, formic acid, tartaric acid. If however higher molecular alcohols are employed in my process, such as amyl alcohol or higher ones which are not miscible with water to any appreciable extent, I prefer the employment of acidic catalysts which are insoluble in water. Examples for this are partial phosphoric, phthalic, oxalic, tartaric esters, particularly of long chain alkyls with four or more carbon atoms. The employment of water soluble acids etc. can be troublesome in cases where water separates from the reaction mixture to such an extent that a second (aqueous) phase is formed; this frequently takes place when large proportions of long chain alcohols are employed. The modification mainly with long chain alcohols is facilitated by adding small proportions of medium sized alcohols which partly are soluble in water, such as butyl alcohol, at the beginning of the second step of my process, proportions ranging from about $\frac{1}{4}$ – $\frac{3}{4}$ parts on each part of the condensation product being suitable.

In my process I prefer the use of alcoholic substances carrying primary alcoholic groups. The proportion of the alcoholic compound may be varied to a great extent, mostly depending upon the degree of modification aimed at. In some cases relatively small proportions suffice, such as about equal parts by weight of alcohol and condensation product primarily formed, and solutions are obtained which may directly serve as varnish bases. In other cases I even employ ten and more parts of the alcohol per one part of urea.

Generally I prefer to eliminate the water being present at the beginning of the second step of the process and formed in the course of the latter, by simple distillation. This elimination is also necessary if a far reaching modification (etherification) is aimed at.

I have further found that part of the formaldehyde which has entered the condensation product obtained during the first step of my process, is relatively loosely bound and may be reacted with urea which I add during the second step, i. e. in the alcoholic, slightly acidic medium. The total molecular proportion however, must not exceed $\frac{1}{2}$ molecule of urea per each molecule of formaldehyde for otherwise precipitates in the reaction mixture or at least turbidity may be formed.

The properties of the end products obtained according to my process may be varied to a large extent, depending upon the conditions employed. Viscous or solid resins generally are obtained if relatively small proportions of alcoholic compounds are employed. These products, as a rule, are thermosetting; they may be employed together with alkyd resins for stove drying or also for self-hardening varnishes. The films obtained are distinguished by excellent resistancy also against water. By prolonged treatment with large proportions of the alcoholic compounds viscous or sticky end products can be obtained which are entirely stable in the heat, and when long chain alcoholic compounds e. g. having 6

and more C atoms, are employed, also in the presence of strong acids, which fact distinguishes these products over the urea formaldehyde resins heretofore known. In order to achieve products of this type I prefer a total molecular ratio of about 3 or more molecules of formaldehyde bound per each molecule of urea. Resins obtained in this way are compatible in any proportion not only with cellulose esters and cellulose ethers, but also with fatty oils, stand oils, acrylic acid esters, vinyl resins, styrene resins, chlorinated rubber so that they may serve as plasticizing agents in varnishes of nearly any kind or in plastic masses.

Although I specially referred to ordinary alcohols hereinbefore I wish to be understood that compounds carrying other groups besides the alcoholic hydroxy group, such as partially etherified or esterified polyhydric alcohols, chlorinated alcohols, olefinic alcohols may also be employed.

My invention may be better illustrated by the following examples although the invention is not limited thereto:

Example 1

60 grams of urea, 240 grams of formaldehyde and 1.2 grams of KOH are heated to 60° C and, in the course of two hours, the temperature is raised to 80° C and kept for about another hour. Thereupon the solution is carefully neutralized by addition of phosphoric acid and is subjected to distillation at diminished pressure at a temperature between 60 and 80° C. About 144 grams of a clear or only slightly turbid, sirupy resin almost free from water are obtained. The distillate contains 3.6 grams of formaldehyde. 175 grams of ethyl alcohol, propyl alcohol or butyl alcohol and such an additional quantity of phosphoric acid is added as to secure a pH of 5 to 5.5. The whole mixture is heated under reflux until, except a small quantity of salts formed, it appears perfectly clear which is the case already after a short time. Thereupon 15 to 20 grams of urea are added and heating is continued under reflux or in a closed apparatus for several hours until the solution of the resin formed yields a quickly setting film. The product obtained may serve as a varnish. The properties of the varnish may be varied by adding e. g. a castor oil modified alkyd resin; such a varnish is well suited as a base for stove drying enamels.

Example 2

The solution of 100 parts of urea in 500 parts of aqueous formaldehyde (40% vol.) after reducing the acidity to a pH of 5.5 by addition of an alkali, is heated for several hours to 80–85° C. When subjected to distillation in vacuo at the same temperature, 268 to 270 parts of a viscous, perfectly clear, colorless resin are obtained. The resin, when heated in thin layer during several hours to 60–70° C, practically does not suffer any loss in weight. It is soluble in any proportion not only in water but also in ethyl alcohol, and, to a restricted proportion, also in butanol.

In the distillate about 11 to 14 parts of formaldehyde can be established which fact proves that the weight of the resin obtained almost exactly corresponds to the total amount of the components which entered into reaction.

By mixing the resin on a kneading machine with 50 parts of urea until complete solution, if necessary with the aid of heat, a product is obtained which, when heated for a prolonged period

of time at temperatures of about 100°C., is gradually converted into high molecular stages and finally into the unmeltable condition. Of course heating may be discontinued at any desired still soluble stage.

A resin soluble in hydrocarbons may be obtained in the following way: The condensation product initially formed is heated together with 500 parts of a mixture of higher alcohols e. g. derived from the catalytical interaction of H₂ on CO under pressure. A suitable proportion e. g. of formic acid or of a partial alkyl phosphoric ester is added in order to secure a pH between 5.2 and 5.6. After reacting for about one hour at about 100° C, 40 to 50 parts of urea are added, whereupon the temperature is gradually raised and the water formed during the reaction driven off. The alcoholic upper layer of the distillate is reintroduced into the reaction mixture, and this procedure continued until about 35 to 38 parts of water have been collected. When concentrated to a solid content of about 65% the highly viscous resin solution may be diluted by hydrocarbons of any kind without causing turbidity. It may be employed together with alkyd resins for stove drying or also for self-hardening varnishes. The films obtained are distinguished by excellent resistancy also against water.

Example 3

A solution of 60 grams of urea in 450 grams of formaldehyde (30% by weight) after being nearly neutralized by means of barium hydroxide (pH about 6), is heated for several hours until a sample shows that 4 mols of formaldehyde are bound. After concentrating the reaction mixture under

diminished pressure 60 grams of butyl alcohol or amyl alcohol and a sufficient quantity of phosphoric acid are added as to completely precipitate the barium as phosphate. Heating is continued on the boiling waterbath until the reaction mixture has become clear. This process may be accelerated by adding a small portion of a partial phosphoric ester or another acidic compound insoluble in water but soluble in alcohols. Then 900 grams of n-octylalcohol and all together 1.5 grams of partial phosphoric esters obtained by the action of P₂O₅ on octyl-alcohol in excess, are added in order to bring about a pH of about 5.5. Finally the filtered solution is heated and subjected to distillation for several hours at 140°C. The octyl-alcohol which did not enter the reaction and mainly remains in the reaction mixture during the preceding treatment is finally removed e. g. by distilling under vacuo.

About 400 to 420 grams of a pale yellow, oily condensation product are obtained being readily soluble both in alcohols and in hydrocarbons of any kind. It may serve as a plasticizing agent in varnishes or in plastic masses. Its complete stability on heating or in the presence even of strong mineral acids is particularly noteworthy and distinguishes the product over the urea formaldehyde resins heretofore known.

The n-octylalcohol may be replaced by a branched primary alcohol or a mixture of e. g. hexyl to decyl alcohols such as derive from CO+H₂ high pressure synthesis, or which may be obtained by catalytical hydrogenation of high molecular aldehydes of the aldol synthesis.

HERBERT HÖNEL.

ALIEN PROPERTY CUSTODIAN

HYDRATION OF OLEFINES

Henri Martin Guinot, Niort, France; vested in the
Alien Property Custodian

No Drawing. Application filed January 8, 1941

In the industrial practice, available olefines are mostly accompanied with an important proportion of corresponding saturated hydrocarbons the separation of which for the purpose of isolating the pure olefine presents certain difficulties due to the close similitude of boiling points.

It is therefore advantageous to be able to treat directly such mixtures, in gaseous phase or in liquid phase, in order to hydrate olefines contained therein having preliminarily to separate different components thereof.

It has already been proposed to treat directly such mixtures, particularly propane-propylene fractions obtained by rectification of cracking products of crude petroleum oils, by means of hydrating solutions, such as concentrated sulphuric solution, in order to absorb olefines comprised therein. The solutions obtained are then diluted in order to bring about the hydrolysis of alcoyl sulphuric acids transitorily formed. The liberated alcohols are finally isolated by suitable means, for example by distillation or extraction by means of solvents.

However, the processes heretofore propounded present many disadvantages, the principal ones residing in the impossibility of bringing about a complete exhaustion in olefine of the mixture of hydrocarbons by the hydrating solution, owing to an inadequate treatment, and in the necessity of putting in highly concentrated sulphuric solutions the recovery of which is costly and involves decreases in the yield of alcohols, the latter being partially destroyed in the course of regeneration.

The present invention, while from different points of view improving technical means heretofore set forth, permits of eliminating aforesaid inconveniences and of obtaining excellent results.

The process, object of this invention, substantially consists first in liquefying the mixture of hydrocarbons and then in bringing about in an absolutely methodical manner the exhaustion within a battery of absorption. Such battery comprises a certain number of decantation elements interconnected by means of vertical pipings which permit of causing both the mixture of hydrocarbons to be hydrated and the hydrating solution to circulate in a counter-current; such circulation is ensured by means of blowing in an inert gas preliminarily compressed. At the ends of the battery there are gathered, on one part, a liquid constituted by saturated hydrocarbons, practically free from olefine and employable for any suitable purpose, and, on the other part, a hydrating solution, saturated with olefine and

containing alcohol caused to appear therein by dilution and heating.

The intimate contact between the mixture of hydrocarbons and the hydrating solution is ensured in the very course of the upflow by the inert gas; this permits of doing away with various means for intense mechanical stirring which have been employed in the most of prior processes and theretofore considered as absolutely necessary. It was then impossible to foresee that the short contact between the two liquids in a piping system designed for their upflow would have been sufficient for obtaining a rapid action of the hydrating liquid upon the diluted olefine.

The hydrating solution, hydrolysed at the outlet end of the battery for causing the alcohol to appear, is completely exhausted in this compound within a still of any suitable type scavenged from its bottom to its top by a current of hot inert gas. In this manner, the regeneration of the acid by concentration in the hot way is carried out in the absence of any trace of alcohol, whereby inevitable destructions inherent to prior processes are avoided. Thus, the formation of coal products is prevented and the initial effectiveness of hydrating bath is almost infinitely maintained.

In order to show how the invention may readily be carried into practical effect, the same will now be described with reference to the accompanying drawing which diagrammatically illustrates one embodiment thereof and is not to be construed in a limiting sense.

This drawing, in one sole Figure, schematically shows an olefine hydrating plant according to the present invention.

The absorption portion of this plant comprises a series of decantation elements $D_1, D_2 \dots D_n$, the number of which varies according to the nature of the mixture to be treated, the rate of concentration of hydrated acid and operative conditions selected. These decanters are interconnected by means of suitable pipings which will be described further below. Respectively adjoined to each decanter is a gas exhaust head $G_1, G_2 \dots G_n$. The whole battery operates under a pressure made sufficient to maintain the mixture of hydrocarbons in liquid state at a temperature under consideration.

A compressor C permits of bringing to the necessary pressure the inert gas serving to effect the upflow. This gas is stored in a tank B from which it is supplied to emulsion vessels $E_1, E_2 \dots E_n$ by means of a pipe M and pipes $t_1, t_2 \dots t_n$ provided with suitable valves.

A collecting conduit N permits of recovering the

gas which has served for the upflow in the different elements, and of directing the same back to the compressor C through the medium of a separator S and pipe 2.

The liquid mixture of hydrocarbons to be treated and contained in a tank P is introduced through a pipe P_n into one end of the battery, while the hydrating solution, for example an aqueous solution of sulphuric acid supplied from a tank A, is introduced into the other end thereof through a pipe a₁.

The hydrating solution is encountered in the emulsion vessel E₁ by the mixture of hydrocarbons which, being already almost exhausted in olefine and constituting the upper layer in the decanter D₂, arrives at this vessel E₁ through the pipe P₁. Under the action of the inert gas blown in through the pipe t₁ both liquids, under the form of an emulsion, are forced to flow up into the head G₁, wherefrom after separation of the gas the mixture flows into the decanter D₁ and is therein divided into two layers. The upper layer constituted by saturated hydrocarbons practically free from olefine flows out of the system through a conduit h. The lower layer of D₁, constituted by sulphuric acid already comprising a certain proportion of alcoyl sulphuric acid, flows through the pipe a₂ into the emulsion vessel E₂ in which it is encountered by the upper layer of decanter D_n arriving thereat through the pipe P₂. From the vessel E₂ both liquids are caused by the inert gas to flow up into the head G₂ to be thereafter separated in the decanter D₂, and so on from element to element.

In the emulsion vessel E_n the hydrating solution, already charged almost at maximum with alcoyl sulphuric acid, is encountered by a fresh mixture of hydrocarbons outflowing from the tank P. After flowing up into G_n and decanting in D_n the hydrating solution is finally drawn out of the battery through the pipe e.

The chemical phenomena produced in the battery are pretty complex owing to the fact that two reactions take place therein simultaneously but at different velocities, viz :

(a) At first, at the contact with olefine a certain proportion of sulphuric acid of the hydrating solution gets fixed under the form of alcoyl sulphuric acid. This results in a decrease of the free acidity of the bath and, consequently, in a reduction of the titration of the latter, the quantity of water having remained without variation.

(b) Simultaneously there is observed partial hydrolysis of alcoyl sulphuric acid, reaction which not only liberated sulphuric acid, but also produced consumption of water and, consequently, tends to increase the titration of hydrating solution.

Velocities of these two parallel reactions depend upon a certain number of factors and, in particular, upon the temperature of the hydrating bath, its degree of concentration and content in alcoyl sulphuric acid. One therefore ascertains, from one element to the other in the battery, a variation of the free acidity and of the titration defined by the ratio:

$$\frac{\text{free SO}_4\text{H}^2}{\text{SO}_4\text{H}^2 \text{ plus water}}$$

In order to insure the constancy of this ratio, which is necessary for obtaining good results, it is expedient to provide on each element of the battery a water supply adjustable at will; such

water comes from a tank F and is supplied by pipes f₁, f₂ . . . f_n.

At any rate, the hydrating solution charged with olefine flowing out of the battery through the pipe e is slackened in its pressure to the ordinary pressure at O and then submitted in a tank H to a heat and a dilution by water inflowing from a tank I through a pipe 3, for the purpose of hydrolysing as completely as possible alcoyl sulphuric acid comprised therein and liberating alcohol therefrom.

The hydrating solution charged with alcohol is then introduced through a pipe 4 to the upper portion of a still K of baffle plate type or checker pile type travelled from its bottom to its top by a hot inert gas current. The hydrating solution, which falls down from baffle to baffle towards the bottom of such still, gets rid of alcohol and of a portion of water contained therein, whereafter it flows out through a pipe 5 into a boiler L. The latter is provided with heating means and a stirring device R and a strong current of inert gas is blown therein by means of a fan V.

Under the action of said heating and stirring the gas is saturated with water steam, whereby the sulphuric solution in the boiler is caused to concentrate. Such concentration may be adjusted to the desired extent by acting upon the intensity of heating and upon the discharge of inert gas in fonction of the hydrating solution supply. In this way there is effected a perfect regeneration of the hydrating reagent which after cooling at T is reintroduced into the tank A by means of a pump U and pipe 6.

The inert gas charged with water steam penetrates through a conduit 7 into the bottom portion of the still K where, as has been seen, it causes the elimination of alcohol contained in the supplied solution. The gases and steam released at the top of the still K are introduced through a conduit 8 into a condenser Q; at the outlet end 9 of the latter there is gathered hydrated alcohol which may be concentrated in an apparatus of known kind (not shown). The non-condensed gases freed from alcohol and water are then retaken up by the intake end of the fan V, eventually reheated at 10 and then blown again into the boiler L, thereby accomplishing a complete closed cycle.

The invention is not limited to the particular embodiment above illustrated and described, for modifications may be effected therein without departing from the scope of the invention. For instance, instead of separating alcohol by mere condensation, a washing tower may be employed to extract therein the alcohol from the entraining gas by means of a suitable solvent, as is indicated in the French patent No 850,938.

Also, the upflow pipes f₁, f₂ . . . f_n of the battery may be encased with a view to regulating the temperature of reaction.

It may also be advantageous to make the upflow pipes of unequal length in different elements throughout the battery with a view to compensating, by conveniently timing the contact, for variations in the reaction velocity from one point to the other of the battery.

Neither will the scope of the invention be departed from by the recovery of heat between certain elements of the plant. In particular, there may be utilised hot water from the tank Q or T, or both, for reheating the gas at 10.

It may also be advantageous to provide in the still K one or more intermediate evaporators to

insure reheating of the hydrating solution in the course of its exhaustion in the said still.

Example

It was proposed to manufacture isopropyl alcohol from a liquid mixture constituted by:

	Per cent
Propane -----	80
Propylene -----	20

The operation was effected in the plant pre-
cedingly described and the operative conditions
were as follows:

Hydrating solution: SO^4H^2 at 75%;

Number of elements in the battery: 12;

Temperature in the battery: 40° cent.;

Pressure: 20 kgs/sq. cent.;

Nature and pressure of the inert gas for up-
flow;

Nitrogen at 25 kgs/sq. cent.;

Discharge of liquid propane-propylene mix-
ture introduced into the battery through Pn;

500 kg/hour;

Discharge of hydrating solution entering into
the battery through a_1 :

850 kgs/ hour;

Hydrolysis of the hydrating bath leaving the
battery:

Dilution at 50% and heating at 80° cent. for one
hour;

Inert gas employed in the phase of concentra-
tion-desalcoholization:

Hydrogen;

Regeneration temperature of the acid in L:

120° cent.;

The following results were obtained:

Discharge and purity of propane leaving the
battery through h :

400 kgs of propane containing less than 0.25%
propylene;

Discharge of isopropyl alcohol gathered
through 9:

139 kgs meant pure;

Efficiency: 97,5%

Although the above stated example was rele-
vant to the treatment of the propane-propylene
mixture, the present invention is in no way lim-
ited to the treatment of such mixture and is as
well applicable to other homologous products, in
particular to butane-butylene mixtures.

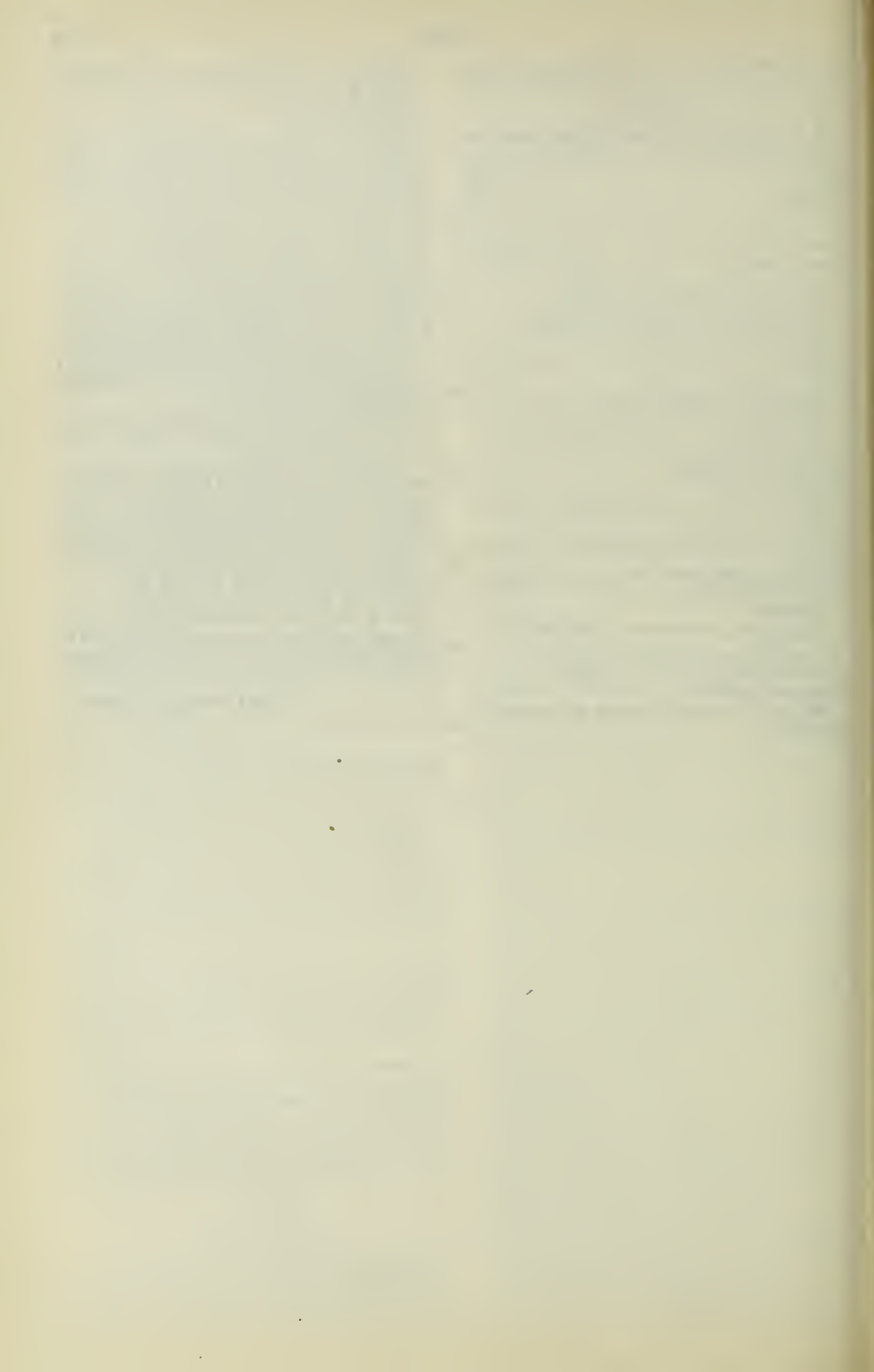
According to the present process there may
also be treated mixtures comprising saturated and
not saturated hydrocarbons having a different
number of carbon atoms, such for example as
mixtures containing hydrocarbons having 3 and
4 carbon atoms. Different alcohols formed will
be simultaneously eliminated by the gaseous cur-
rent in the still K and there will be gathered at 9
a mixture of corresponding alcohols which will be
separated by ordinary means.

Finally the invention is applicable to mixtures
rich in olefines and comprising but some percents
of saturated hydrocarbons.

As a gas to serve for the operation of the bat-
tery, there may be employed hydrogen instead of
nitrogen, or else hydrocarbons, saturated or not
saturated, under the only condition that they be
gaseous and practically without action upon the
hydrating solution selected within ranges of tem-
perature and pressure under consideration, for
example, methane, ethane, ethylene, etc.

Identically as to the inert gas employed in the
phase of regeneration-desalcoholization, but in
this case it will be advantageous to make use of
a light gas having the best qualities with regards
to the calorific exchange, for example hydrogen.

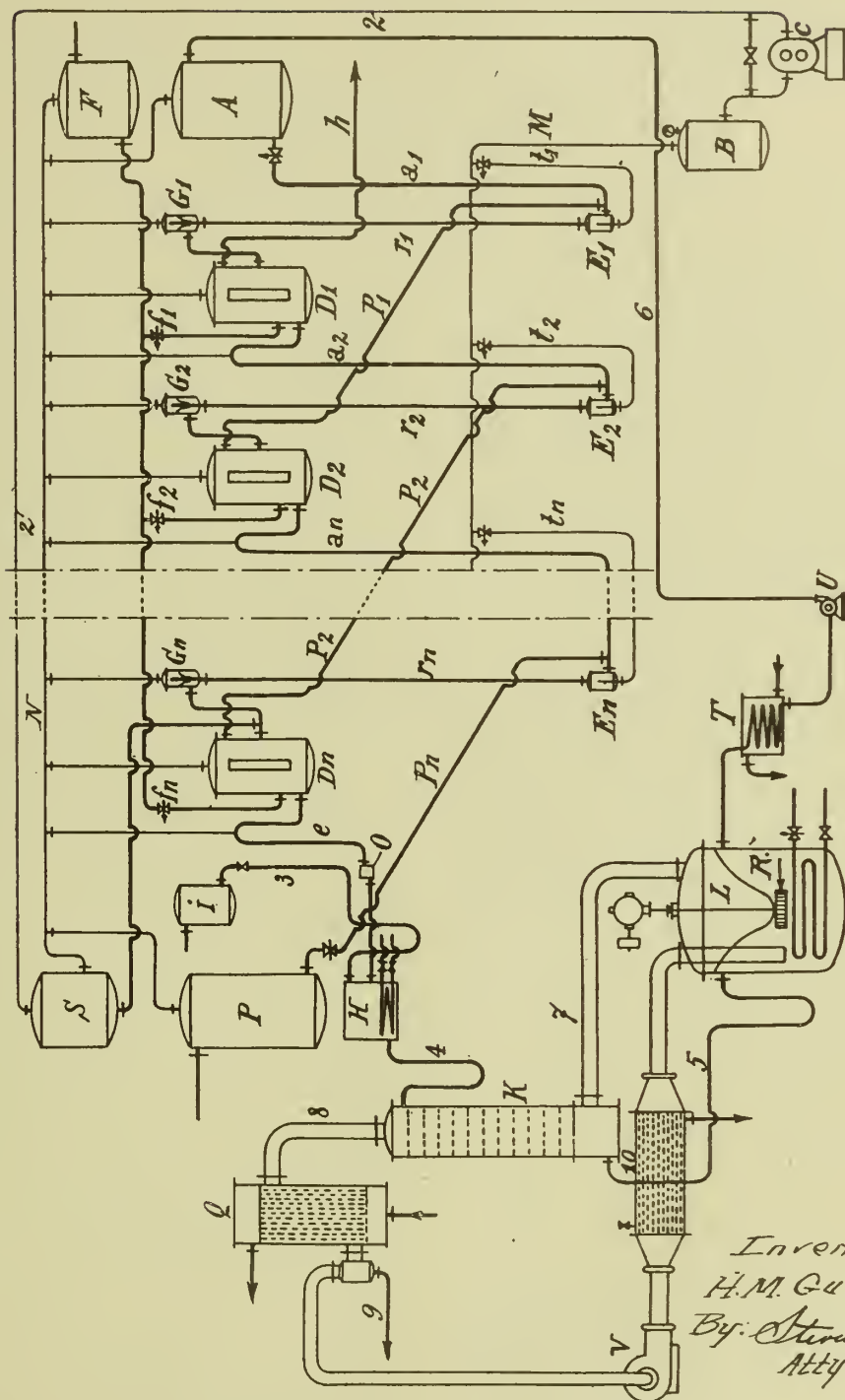
HENRI MARTIN GUINOT.



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Inventor:-
H. M. Guinot
By: *Stevens & Blaine*
Attys.



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METHOD OF INFLUENCING THE POLYMERIZATION AND THE PROPERTIES OF THE OBTAINED PRODUCTS

Willy O. Herrmann, Deisenhofen, and Wolfram Haehnel, Munich, Germany; vested in the Alien Property Custodian

No Drawing. Application filed January 13, 1941

Surprisingly it has been found that polymerization reactions and the polymers obtained thereby may be influenced by an addition of vinyl crotonate. Thereby the grade of polymerization increases so much as not known until now, and the properties of the polymers vary in a wide range, whereby even unknown properties may be obtained. Herein lies the technical value of this invention and its significant progress.

Until now, it was impossible to produce a vinyl acetate insoluble in all solvents. The use of vinyl crotonate according to this invention solves this problem. Furtheron it is also possible to produce the most various polymers out of the same monomeric starting material, e. g. vinyl acetate, though exactly the same condition and the same apparatus are applied. In order to obtain these various polymers, it is only necessary to vary the amount of the added vinyl crotonate, whereby even very small amounts of this substance change the properties of the polymers. In such a way polymers of a desired solubility, capability of swelling, and a determined melting point and various thermoplasticity are attainable.

The described effect of vinyl crotonate upon the polymerization of vinyl acetate is also attainable if other polymerizable compounds like other vinyl or acrylic compounds or mixtures of polymerizable compounds are subjected to polymerization in the presence of vinyl crotonate.

This discovery of the surprising and specific effect of vinyl crotonate seems also to clear up some striking facts: e. g. the higher activity of vinyl acetate which was produced in former times and the insolubility of the polymers in spirit are probably due to the presence of an insignificant amount of vinyl crotonate. Hence follows that later on when vinyl acetate could be produced in a pure state, the activity of vinyl acetate and the insolubility of the polymers in spirit disappeared, and that it was necessary to discover the effect of vinyl crotonate in order to obtain the mentioned properties.

The polymers obtained according to this invention may not only be applied in the known way but also in a wider range, which is determined by the new attainable properties of the polymers like insolubility, larger mechanical capability of resistance, infusibility, diminished thermoplasticity, absence of cold flow and so on. E. g. the vinyl acetates according to the invention can now be also applied for the production of pressed articles and the like, if a small thermoplasticity is desired.

Example 1

Monomeric vinyl acetate mixed with the same volume of alcohol was polymerized under addition of 1% of benzoylperoxide (calculated upon the applied vinyl acetate). In a quiet course of polymerization a polyvinyl acetate, solved in alcohol, was obtained which is soluble in acetone, benzene, acetic ester, and many other solvents, melting at 110°.

If the experiment was repeated in the presence of 1% of vinyl crotonate the polymerization took place very violently. The polymer precipitated in form of a gelatinous mass and was infusible and insoluble in solvents.

Example 2

5 mixtures of 30 per cent by volume of spirit and 70 per cent by volume of vinyl acetate were polymerized with 1% of benzoylperoxide by heating. Thereby 1, 2, 3, 7 and 10% vinyl crotonate, calculated upon the applied vinyl acetate, were added. The result was that the obtained polymers had various melting points and various capabilities of swelling. In the following table, the numbers mentioned under "capability of swelling" means volume relation in per cents between the swelled and non-swelled material.

Vinyl crotonate added per cent	Capability of swelling			Melting point
	In spirit	In acetone	In benzene	
1	(1)	(1)	(1)	115
2	(1)	(1)	(1)	195
3	463	1,093	1,098	(2)
7	384	885	807	(3)
10	273	825	724	(2)

1 Soluble.
2 Infusible.

Example 3

Pure vinyl acetate was enclosed in glass tubes and polymerized under an addition of 1 or 10% vinyl crotonate by sun light. Infusible polymers, insoluble in alcohol, acetone and benzene were obtained. Following a table about the capability of swelling as in example 2.

Vinyl crotonate added per cent	Capability of swelling		
	In spirit	In acetone	In benzene
1	217	639	458
10	157	356	332

In the absence of vinyl crotonate, products are obtained which are hardly soluble in spirit but soluble without any difficulty in acetone and benzene.

Example 4

2 mixtures consisting of 9 parts by weight of ethyl alcohol and 21 parts by weight of vinyl formate were polymerized by heating with 0.2 parts by weight of benzoylperoxide, whereby in one case 0.2 parts by weight of vinyl crotonate were added. The solubility of the polymers differs as follows:

	Made with vinylcrotonate	Made without vinylcrotonate
In acetone	Insoluble	Soluble.
In formic acid	do	Do.
In chloroform	do	Do.
In dioxane	do	Do.
In acetic acid	do	Do.
In pyridine	do	Do.

Example 5

56 g of monomeric vinyl chloride solved in 500 g of methyl alcohol were polymerized by active light whereby the formed polyvinylchloride was obtained in a form of a white powder. The polymer was clearly soluble in hot and cold dioxane. The same polymerization in the presence of 0.56 g vinyl crotonate yielded a polymer unsoluble even in boiling dioxane.

Example 6

240 g of monomeric vinyl acetate were emulsified under stirring with 200 g of a aqueous solution of polyvinyl alcohol of 6%. The emulsion was polymerized by slow heating in the presence of 1 ccm of hydrogen peroxide of 30%. The polymer, an emulsion of polyvinyl acetate which may be diluted homogeniously with water, yielded with methyl alcohol a clear solution.

A repetition of this polymerization in the presence of 2.4 g of vinyl crotonate yielded a coarse-grained paste which could not more homogeniously diluted with water and the substance of which was not soluble in methanol.

The same polymerization in the presence of 0.5 g of vinyl crotonate yielded an emulsion which could be diluted homogeniously with water. But after some hours a precipitate was formed which was nearly not soluble in methyl alcohol.

In this way the physical character of an emulsion and its behaviour against solvents may be varied in a wide range.

Example 7

A mixture of 86 g of vinyl acetate and 263 g of trichloroethylene was boiled in the presence of 5.2 g of benzoylperoxide for 5½ hours whereby the co-polymerization of the two unsaturated monomers passed various intermediate stages and finally gave a mixed polymer with the brutto formula of $C_6H_7O_2Cl_3$. By purification with water steam and by precipitating the solution in acetone with water, a polymer was obtained in the form of a white, light powder. This product easily solves in many organic solvents, specially in ether and methylalcohol.

The same polymerization in the presence of 0.9 g of vinyl crotonate yielded a co-polymer hardly solving in ether and unsoluble in methyl alcohol.

It will be understood, of course, that the invention is not limited to the special amounts of applied vinyl crotonate set forth in the examples for the purpose of disclosure, but is capable of considerable modification of this amounts. The effect of vinyl crotonate according to this invention is attainable with amounts of 0.1 to a few per cent of this substance. The more vinyl crotonate is applied, the more increases the molecular weight of the obtained polymers. But there has been found, that an addition of more than a few per cent of this substance does not increase the effect but yields co-polymers of vinyl crotonate with the starting material to be polymerized.

WILLY O. HERRMANN.
WOLFRAM HAEHNEL.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR MAKING ALDOL

Ladislav Szlatinay, Budapest VIII, Hungary;
vested in the Alien Property Custodian

No Drawing. Application filed January 18, 1941

There are known several processes for making aldol from acetaldehyde, based on the knowledge that acetaldehyde in an alkaline medium is converted into aldol. With these processes either a strong alkali (e. g. sodium hydroxide) or some salt or compound of weaker alkalinity (sodium carbonate, strontium oxide, calcium oxide, etc.) has been used. The use of a strong alkali has, however, the disadvantage that the reaction starts quickly, the acetaldehyde easily and suddenly boils, during which a great part of it evaporizes, while another part is converted into a thick, even hard aldol resin (poly-aldol), which is no more apt for further synthesis. Even if the sodium hydroxide is added with the greatest care and only with a very small surplus, even then we shall obtain a relatively great quantity of such poly-aldol which is of no use for further synthesis. If a weak alkaline medium is used conversion will be very slow, but even then it may happen that the aldol formed at the start of the reaction polymerises into poly-aldol before the remaining acetaldehyde is converted in the course of the reaction.

Two problems must therefore be solved for making good quality aldol. On the one hand we had by slowing down the reaction and by con-

ducting it cautiously to prevent the boiling of the acetaldehyde before time, on the other hand it had to be prevented to let the acetaldehyde once converted into monoaldol polymerise.

5 We have found that both the regulation of the course of the reaction and the prevention of the polymerisation of the aldol can be attained, if we add to the reaction mixture while making the aldol polyvalent phenoles, e.g. hydroquinon, 10 pyrogallol, etc. It has been known that such polyvalent phenoles are compounds preventing polymerisation, they are so-called inhibitors and have already been used in the past, to prevent further polymerisation mainly of the ready made 15 styrol-polymerisates while these are standing. Owing to their strong stabilising effect, however, they have hitherto not been used in connection with the making of aldol, since it was presumed that due to this feature the same would prevent 20 the conversion of acetaldehyde into aldol. Against this we have found that e.g. the addition of hydroquinon does not prejudice the condensation process, but it furthers the uniform course of the reaction and wholly prevents the aldol becoming resinous while the same is made 25 from acetaldehyde.

LADISLAV SZLATINAY.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR MAKING ALDOL

Ladislav Szlatinay, Budapest, VIII, Hungary;
vested in the Alien Property Custodian

No Drawing. Application filed January 18, 1941

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Two problems must therefore be solved for making good quality aldol. On the one hand, we had by slowing down the reaction and by conducting it cautiously to prevent the boiling of the acetaldehyde before time on the other hand it had to be prevented to let the acetaldehyde once converted into monoaldol polymerise.

We have found that both the regulation of the course of the reaction and the prevention of the polymerisation of the aldol can be attained if we maintain in the weakly alkaline medium used for making the aldol a practically constant hydrogen ion concentration by obtaining alkalisations through a suitable buffer solution. An example of such a buffer solution is a mixture of sodium tetraborate and sodium hydroxide the pH of which is 11-12. The actual hydrogen ion concentration of the acetaldehyde made alkaline with this solution is much more constant than if either sodium hydroxide or some other weak alkali is used.

We can still more efficiently realise the regulation of the course of the reaction according to the invention and the prevention of the poly-

merisation of the aldol, if we add to the reaction mixture during the making of the aldol according to the above process according to our Application No. . . . polyvalent phenoles, e. g. hydroquinon.

An example of the process is given as follows: 1 kg of possibly fresh acetaldehyde, distilling at 21-24 C° is cooled down to 0° and then carefully made neutral with a solution of n/2 or n/5 sodium hydroxide by using a phenolphthalein indicator. Care must be taken that during this procedure temperature should not increase above 10 C° and the addition of sodium hydroxide is stopped after the solution has kept its red colour for 4-5 minutes. Thereafter we slowly drop in during stirring or shaking the buffer solution which consists in a mixture of 50 cm³ of n/10 sodium tetraborate and of 10 cm³ sodium hydroxide. After having dropped in the buffer solution 10-15 gr of hydroquinon are added and exchanging continuously the outer cooling water for an always warmer one, we slowly heat the reaction mixture to 40 C°. If we proceed carefully we shall attain the 40 C° without the solution boiling at all. About 1½ to 2 hours are required for the operations described and for 7-8 hours from the end of these operations the mixture is kept at 40 C°. During this time neither stirring nor shaking are needed so that the maintenance of the inner temperature of 40 C° requires small supervision. After 9 hours from the start of the reaction the solution is neutralised by using n/2 or n/5 HCL in the presence of a BTB (brome thymol blue) indicator to a green colour and after one or two days standing it is distilled in vacuum.

Vacuum distillation is made under a slow, successive increasing of the temperature and successive decreasing of the pressure as in this way we shall obtain from the 1 kg of acetaldehyde mentioned as example—together with the aldol convertible from the pre-distillate according to the above process—about 700-750 gr of such mono-aldol the boiling point of which at a pressure of 2-3 mm is between 75-84 C° and which in further synthesis will behave according to the formula $\text{CH}_3\text{CHOHCH}_2\text{—CHO}$.

LADISLAV SZLATINAY.

ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING DIOLEFINES

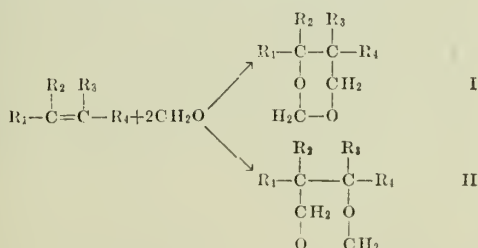
Wilhelm Friedrichsen, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 5, 1941

The present invention relates to an improved method for the production of diolefins, in particular aliphatic diolefinis hydrocarbons having conjugated double linkages.

I have found that aliphatic diolefinic hydrocarbons having conjugated double linkages are obtained in a simple manner by contacting 1,3-dioxanes which are substituted at least once in the 4- or 5-position by the radicle of a hydrocarbon of the paraffin series in the gas phase with solid catalysts promoting the splitting off of water in the presence of vaporized organic compounds which are liquid under ordinary conditions and which do not decompose under reaction conditions.

The 1,3-dioxanes serving as starting materials according to my invention may be prepared from monoolefinic aliphatic hydrocarbons by the action of formaldehyde in the liquid phase in the presence of an acid catalyst. The reaction is preferably carried out in an inert solvent, such as water, benzene, toluene or halogenated hydrocarbons, such as methylene chloride or dichloroethylene, at temperatures between room temperature and about 150° C. Suitable acid catalysts are in particular mineral acids, such as hydrochloric acid, phosphoric acid or sulfuric acid, or acid reacting salts, such as zinc chloride. Suitable olefines are straight-chain or branch-chain aliphatic olefines, such as propylene, n-butylene, n-hexene, iso-butylene, iso-amylene, iso-hexene and their higher homologues. The formation of 1,3-dioxanes may be explained according to the following equations:



wherein R₁ stands for a paraffinic hydrocarbon radicle, and wherein R₂, R₃ and R₄ stand for hydrogen or paraffinic hydrocarbon radicles. The dioxanes corresponding to formula I constitute the main products.

The 1,3-dioxanes containing in the dioxane ring a carbon atom attached to three carbon atoms and one oxygen atom or a carbon atom attached to four carbon atoms may also be prepared by heating a tertiary aliphatic alcohol with

formaldehyde in the presence of an acid catalyst under the reaction conditions as described above for the preparation of 1,3-dioxanes from olefines.

As solid dehydrating catalysts promoting the conversion of 1,3-dioxanes into 1,3-diolefines there may be mentioned in particular those which have proved suitable for the preparation of unsaturated hydrocarbons from alcohols. These are especially phosphoric acid salt catalysts having an acid reaction under the reaction conditions such as the salts of oxygen acids of phosphorus which have been proposed as catalysts in the U. S. patent 1,841,055 and which include not only the so-called acid salts of the various phosphorus acids but also such neutral salts as have an acid action under the reaction conditions. Silicic acid gel or aluminum oxide are also suitable.

The temperatures to be maintained lie, generally speaking, between about 150° C and 450° C, advantageously between 200 and 300° C. It is preferable, though not necessary, to use an inert diluent, such as nitrogen or steam in addition to the vaporized organic compound which is liquid under normal conditions.

Suitable organic liquids are in particular such compounds which are inert under the reaction conditions, as for example, aliphatic and aromatic hydrocarbons, such as n-hexane, iso-hexane, cyclohexane and its homologues, benzene and its homologues or liquid mixtures of hydrocarbons, or halogenated hydrocarbons, such as tetrachlor methane. There may also be used as the organic diluent the 1,3-dioxanes themselves. This may be done by passing the vaporized 1,3-dioxane with such a speed through the reaction chamber that only part thereof is decomposed, the remaining part leaving the chamber unchanged.

The amount of the vaporized liquid may vary to a considerable extent. There may be used one, two, five or six molecular proportions thereof for each molecular proportion of the 1,3-dioxane to be converted. I prefer to lead the vaporized organic compound in a cycle, by separating it from the reaction products after the reaction gases have emerged from the reaction vessel. Generally speaking, these vapors may be easily separated into the constituents, e. g. into the diolefine, water and formaldehyde and the organic liquid diluent, by fractional distillation.

The following examples illustrate certain ways in which the principle of my invention may be applied, but are not to be construed to limit the invention. The parts are by weight, unless otherwise stated.

Example 1

100 parts of anhydrous primary sodium phosphate are dissolved in 40 parts of water and mixed with 8 parts of primary n-butylamine phosphate together with 20 parts of graphite. The product is then evaporated while stirring and the solidified mass is finally heated to 160° C. After cooling down, the mass is broken up into pieces of the desired size and is screened, and the granules thus obtained are employed as the catalyst.

500 cubic centimeters of a mixture consisting of 3 parts of n-heptane and 1 part of the crude reaction product obtained by condensing isobutylene with an aqueous formaldehyde solution in the presence of phosphoric acid, which product contains 69 per cent of 4,4-dimethyl-1,3-dioxane, 20 per cent of tertiary butyl alcohol, 10.2 per cent of water and 0.8 per cent of higher boiling constituents are vaporized per hour and led with 120 grams of steam over 4.5 liters of the catalyst at 250° C. The vapors emerging from the catalyst are condensed and the condensate led into a column in order to obtain two fractions. The first fraction consists of easily volatile compounds, namely isoprene and isobutylene formed from tertiary butyl alcohol. The second fraction consists of water containing formaldehyde, heptane and unchanged dimethyl-1,3-dioxane. Heptane

and unchanged dimethyl-1,3-dioxane are separated off, admixed with fresh dimethyl-1,3-dioxane and again led into the reaction chamber. The first fraction is distilled whereby pure isoprene is obtained.

8 956 parts of isoprene are thus obtained from 21 888 parts of dimethyl-1,3-dioxane in the course of 485 hours.

Example 2

1000 cubic centimeters of the crude dimethyl-1,3-dioxane described in Example 1 and 220 cubic centimeters of water are vaporized per hour and the vapors led over 4.5 liters of the catalyst described in Example 1 at 250° C. Less than half of the dioxane is converted under these conditions, the remainder being left unchanged. The vapors emerging from the catalyst are led into a column and separated into two fractions. The first fraction consists of isoprene and isobutylene from which pure isoprene may easily be recovered. The second fraction consists of water, formaldehyde and dimethyl-1,3-dioxane. Water and dimethyl-1,3-dioxane are led back into the reaction vessel.

25 In the course of 100 hours 15 550 parts of dimethyl-1,3-dioxane are thus converted into 6 927 parts of isoprene.

WILHELM FRIEDRICHSEN.

ALIEN PROPERTY CUSTODIAN

KETONES SUBSTITUTED BY MODIFIED PROPIONIC ACID RADICLES AND A PROCESS OF PRODUCING SAME

Georg Wiest, Ludwigshafen-on-Rhine, and Heinrich Glaser, Bonn, Germany; vested in the Alien Property Custodian

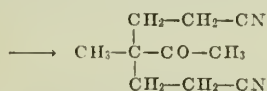
No Drawing. Application filed February 6, 1941

The present invention relates to ketones substituted by modified propionic acid radicles and a process of producing same.

We have found that ketones substituted in α -position to the keto group by two radicles of a nitrogenous functional derivative of propionic acid, may be prepared very easily and with good yields by causing one molecular proportion of a ketone containing in α -position to the keto group at least one CH_2 -group to act on more than one molecular proportion of a nitrogenous functional derivative of acrylic acid, e. g. acrylic acid nitrile or acrylic acid amides, in the presence of an alkaline catalyst.

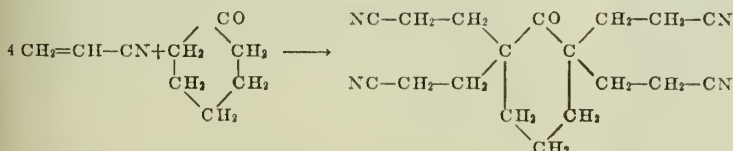
Suitable ketones of the said kind are for example purely aliphatic or cycloaliphatic ketones, such as methyl ethyl ketone, diethyl ketone, methyl iso-butyl ketone, cyclohexanone, methyl cyclohexanone, cyclopentanone, acetyl acetone, acetonyl acetone, and ketones containing aliphatic as well as aromatic radicles, such as ethyl phenyl ketone, phenyl benzyl ketone or benzoyl acetone.

The reaction consists in the addition of at least two molecular proportions of the acrylic acid derivative to one molecular proportion of the ketone and proceeds in accordance with the following equation showing the reaction between acrylic acid nitrile and methyl ethyl ketone:



α -(di- ω -cyanethyl)-ethyl methyl ketone.

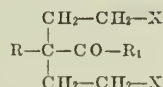
If the ketone used as starting material contains more than one CH_2 -group in α -position to a keto group, there may be added two molecules of acrylic acid derivative for each of those CH_2 -groups. Thus, cyclohexanone may add four molecules of acrylic acid nitrile according to the following equation:



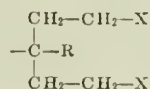
2,6-tetra-(ω -cyanethyl)-cyclohexanone

The reaction products constitute ketones which are substituted in at least one α -position to the keto group by two radicles of a nitrogenous func-

tional derivative of propionic acid. They correspond to the general formula



wherein R stands for an alkyl, aralkyl or aryl radicle, wherein R_1 stands for an alkyl, aralkyl or aryl radicle or for



or wherein R and R_1 may be members of a saturated carboxylic ring, and wherein X stands for a modified carboxylic acid group containing nitrogen, e. g. the nitrile group or an amide group.

In addition to these addition products of two molecules of an acrylic acid derivative to one CH_2 -group, there may be formed as by-products in some cases small amounts of compounds formed by the addition of one molecule of the acrylic acid derivative to one CH_2 -group. Generally speaking, the bimolecular addition products are almost exclusively formed even if using only a slight excess of the acrylic acid derivative over the ketone. Under these conditions only part of the ketone will react, the remaining amount being left unchanged. It is, therefore, preferable to use at least two molecular proportions of the acrylic acid derivative for one molecular proportion of the ketone.

The monomolecular addition products may easily be converted into bimolecular addition products by bringing them into contact with the acrylic acid derivatives in the presence of alkaline catalysts. It is also possible to add these monomolecular addition products to the starting materials used in the practice of our invention.

The addition of the acrylic acid derivatives to ketones containing CH_2 -groups proceeds so

smoothly that the reaction may be started by simply adding one of the starting materials to the other starting material admixed with the catalyst. The reaction proceeds with the evolution of heat. Since the acrylic acid derivatives

are liable to be polymerized at high temperatures, temperatures exceeding about 100° C, preferably those exceeding 70° C should not be used. In order to avoid the polymerization of the acrylic acid derivatives, substances prohibiting the polymerization, e. g. copper or hydroquinone, may be present. If necessary, the reaction mixture has to be cooled during the reaction. When the vigor of the reaction has abated, it may be suitable to gently heat the reaction mixture in order to accelerate the reaction. The reaction may be carried out in the presence of inert solvents or diluents.

Various alkaline substances may serve as the catalyst. Thus, the alkali and alkaline earth metals themselves and their compounds having an alkaline reaction are suitable, for example their oxides, hydroxides or alcoholates. Basic nitrogen compounds may also be used, as for example pyridine. The amount of catalyst to be used may be very small; generally speaking few per cents or less than one per cent thereof, calculated on the amount of the ketone are sufficient. It is not necessary and does not offer any advantage to use an amount corresponding to more than 10 per cent of the acid derivative. When using alkali metals as the alkaline catalyst, the course of the reaction is even unfavorably affected by using large amounts, e. g. more than 50 per cent, of the catalyst.

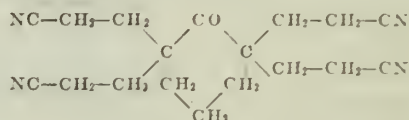
The products obtainable according to our invention may be used for the production of keto dicarboxylic acids by saponifying the modified carboxylic acid group. The esters of these keto dicarboxylic acids are most suitable as plasticizers or solvents.

The following examples will further illustrate how our invention may be carried out in practice. The invention, however, is not restricted to these examples. The parts are by weight.

Example 1

210 parts of acrylic acid nitrile are allowed to

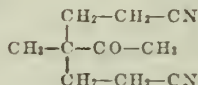
flow slowly at 40° C into a solution of 100 parts of cyclohexanone in 200 parts of benzene, to which 0.2 part of metallic sodium has been added, while stirring. The addition product is formed at once; it deposits in solid form in the course of the reaction. Finally there is obtained a thick pulp of crystals. The crystals are filtered off and washed with methanol. The yield amounts to 250 parts. After recrystallization from glacial acetic acid, the compound melts at 160° C. It contains four molecules of acrylic acid nitrile for one molecule of cyclohexanone and corresponds to the formula:



The same compound may be obtained when replacing the metallic sodium by 1 part of finely divided sodium hydroxide.

Example 2

106 parts of acrylic acid nitrile are allowed to act on a mixture of 72 parts of methyl ethyl ketone with 0.2 part of metallic sodium at 30-40° C while stirring. The mixture is then allowed to stand for some hours. It is diluted with acetone, and carbon dioxide is introduced until it is no longer absorbed. The mixture is filtered off and the filtrate distilled. There are obtained 90 parts of a fraction boiling at 200-203° C. under 1.5 millimeters pressure which solidifies to form crystals melting at 60-62° C. The compound corresponds to the formula:



α -(di- ω -cyanethyl)-ethyl methyl ketone.

GEORG WIEST.

HEINRICH GLASER.

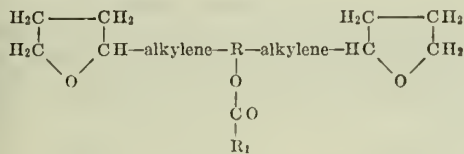
ALIEN PROPERTY CUSTODIAN

SOFTENING AGENT

Ernst Korten, Frankfurt A. Main-Fechenheim, Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 6, 1941

The present invention relates to valuable softening agents more particularly to those of the general formula:



wherein R stands for a member of the group consisting of a methine group and a methine group being a member of the cyclohexane ring and R₁ stands for a radicle selected from the aliphatic and benzene series.

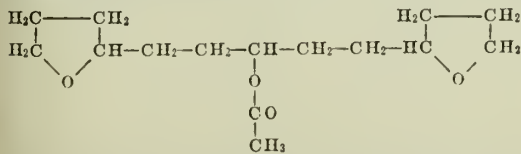
The new softening agents are obtained by condensing two molecular proportions of furfural with one molecular proportion of an aliphatic or cycloaliphatic ketone containing reactive alkyl-groups, entirely hydrogenating the formed condensation products and esterifying the secondary alcohols thus obtained by means of carboxylic acids of the aliphatic and benzene series or their reactive derivatives.

The present new ester compounds exhibit an excellent softening effect on the various thermoplastic compounds of a high molecular weight and the artificial masses obtained therewith, such as highly polymerised vinyl compounds, polyacrylic acid esters and mixed polymerisation products therefrom, moreover cellulosic derivatives.

In order to further illustrate my present invention the following examples are given, the parts being by weight and all temperatures in degrees Centigrade.

Example 1

A mixture of 10 parts of 1.5-ditetrahydrofuryl-3-hydroxypentane and 6.6 parts of acetic acid anhydride is heated for about 2 hours in an apparatus provided with a reflux condenser. Then the formed acetic acid is removed by fractional distillation. Subsequently the reaction product of the formula:

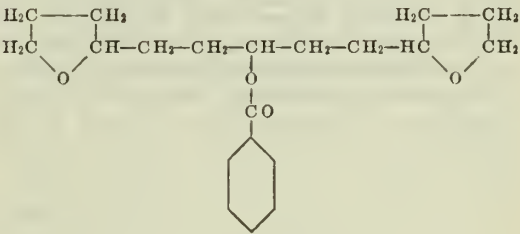


passes over at 1.5mms pressure at 180 to 185° as a colorless and odourless oil, which is not miscible with water.

Corresponding products are obtained when replacing the acetic acid by other aliphatic acids such as caproic, caprylic or capric acid.

Example 2

A mixture of 228 parts of the alcohol as used in example 1 and 250 parts of benzoic acid anhydride is slowly heated at 200 to 220°. When the esterification has been finished the reaction product is digested with a dilute sodium carbonate solution in order to remove the formed benzoic acid. Then the residue is distilled in vacuo. The ester thus obtained of the formula:



boils at 1 mm pressure at 200 to 210° as a viscous, colorless and odourless oil.

Corresponding esters are obtained when esterifying with derivatives of benzoic acid being substituted by methylgroups or halogen.

Example 3

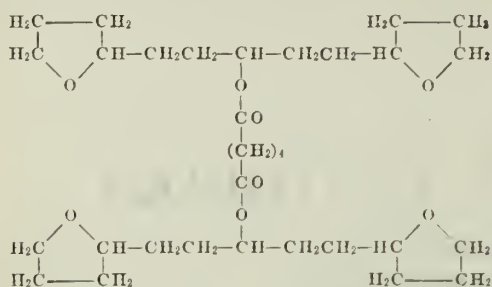
50 parts of the alcohol as used in the foregoing examples are mixed with 40 parts of a mixture of carboxylic acids of acid number 324, obtainable by oxidising the higher alcohols, which are well known by-products of the methanol synthesis. The mixture is slowly heated to 200 to 250° while introducing nitrogen into the reaction vessel. With the nitrogen which passes through also water is removed.

The same ester is obtained according to the following method: A mixture of equal quantities of the alcohol and the aforesaid mixture of carboxylic acids is subjected in the presence of toluene as assistant liquor and a small amount of benzene sulfonic acid to the azeotropic distillation. When the splitting off of water has been finished the reaction product is isolated as described in example 2.

The formed mixture of esters boils at 7 mms pressure at 180 to 240° as a colorless and odourless oil.

Example 4

When esterifying by means of adipic acid the formed diester of the formula:



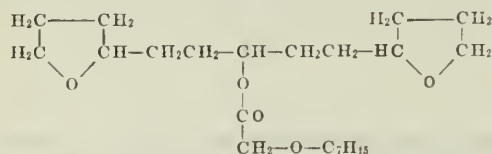
is an odourless oil boiling above 300° at 1.5 mms pressure.

Instead of adipic acid other dicarboxylic acids such as succinic acid may be used as esterifying agent.

In the manner as described in the foregoing examples other entirely hydrogenated condensation products of furfural with suitable ketones such as methylethylketone, diethylketone, cyclohexanone and its alkylated derivatives such as isooctylcyclohexanone yield valuable products by esterification.

Example 5

A mixture of 246 parts of 1,5-ditetrahydrofuryl-3-hydroxypentane and 116 parts of isoheptoxyacetic acid is heated for about 6 hours at about 140° in a vacuo of 20 to 25 mms pressure, the formed water distilling off. Then the temperature is increased during about 6 hours to 180° and the reaction mixture is held at this temperature for 12 hours. The formed ester is isolated by fractionating distillation. The yield is nearly theoretical. The ester thus obtained of the formula:



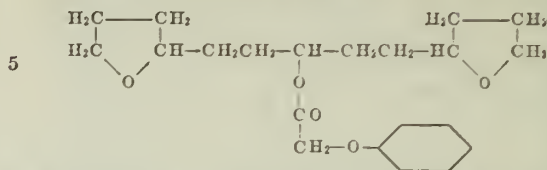
is a colorless and odourless oil, which is not miscible with water and boils at 1 mm pressure at 210 to 215°.

When replacing the isoheptoxyacetic acid by other ethercarboxylic acids derived from alcohols of a lower or higher number of carbon atoms, such as from α -ethylcyclohexanole or from the higher alcohols, which are well known as by-products of the methanol synthesis, very similar esters are obtained.

Example 6

A mixture of 246 parts of 1,5-ditetrahydrofuryl-3-hydroxypentane and 152 parts of phenoxyacetic acid is heated at reduced pressure. With an al-

most theoretical yield by fractional distillation the formed ester of the formula:

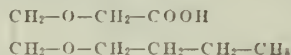


10 is obtained as a colorless and odourless oil, which boils at 223 to 226° at 0.7 mm pressure and is not miscible with water.

A similar ester is obtained when using the phenoxy propionic acid as esterifying agent.

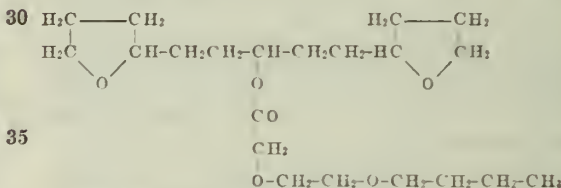
Example 7

By condensing the alkali metal compound of glycolmonobutylether with the sodium salt of monochloroacetic acid there is obtained the dietheracetic acid of the formula:



boiling at 15 mms pressure at 163 to 165°.

176 parts of this acid are mixed with 246 parts of 1,5-ditetrahydrofuryl-3-hydroxypentane and the mixture is heated at reduced pressure. With an almost theoretical yield the ester of the formula:

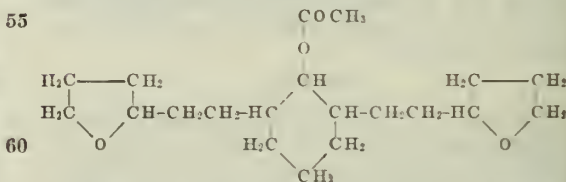


is obtained as a colorless and odourless oil, which is not miscible with water and boils at 0.5 mms pressure at 215 to 220°.

The ethercarboxylic acid derived from glycolmonophenylether yields an ester of similar properties.

Example 8

300 parts of 2,6-ditetrahydrofurfuryl-cyclohexanol obtainable by hydrogenating the yellow condensation product of two molecular proportions of furfural and one molecular proportion of cyclohexanone are mixed with 400 parts of acetic acid anhydride and the mixture is heated under reflux for about 3 hours. By a fractionating distillation with an almost theoretical yield the formed ester of the formula:



is obtained as a colorless oil boiling at 0.6 mm pressure at 190 to 200°.

ERNST KORTEN.

ALIEN PROPERTY CUSTODIAN

ADHESIVES AND COATING MATERIALS

Eugen Bock, Krefeld-Uerdingen, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed February 11, 1941

This invention relates to a new composition of matter suitable especially as an adhesive or coating material, furthermore the invention relates to the employment of the new composition of matter for the purpose mentioned before.

The use of solutions of nitrocellulose and of celluloid as adhesives is known. These adhesives contain considerable amounts of a volatile solvent for nitrocellulose, for instance acetone, methyl acetate, butyl acetate or the like and may contain also non-solvents, such as aromatic or aliphatic hydrocarbons or chlorinated aliphatic hydrocarbons. The quantity of the non-solvent added remains, however, below the dilution number established for each solvent and mixture of solvents, respectively, that is to say, the ratio which exists between non-solvent and solvent when in a nitrocellulose solution, on addition of the non-solvent, the precipitation of the nitrocellulose just begins. The adhesive power is hardly enhanced by the addition of the non-solvent. The latter is rather added to bring about the desired speed of drying and setting and for reasons of economy.

Now, I have found that it is possible to increase to a surprising extent the stability of the agglutinations obtained by means of adhesives built up on the basis of polyvinyl compounds as well as that of the surface coverings obtained by means of coating materials built up on the same basis, by adding to the solution of the polyvinyl compound in an organic solvent such a quantity of a substance being a non-solvent for the polyvinyl compound and compatible with the solvent as is insufficient for precipitating the dissolved polyvinyl compound. Especially when porous substances, such as textiles or leathers are to be glued or to be coated, the products of the present invention are particularly suitable since they do not penetrate into the pores but remain active at the surface.

As polyvinyl compounds there may be mentioned: polyvinyl chloride, polystyrene, polyvinyl ethers, for example polyvinyl ethyl ether, polyvinyl propyl ether, polyvinyl isopropyl ether, polyvinyl isobutyl ether, if desired as interpolymers of these polyvinyl ethers with vinyl ethers of the higher aliphatic, aromatic or alicyclic alcohols with up to 35 carbon atoms, or of mixtures from alcohols, polyvinyl esters, for example, polyvinyl acetate, polyacrylic acid compounds, such as polyacrylic acid nitrile, polyacrylic acid methyl ester, polyacrylic acid ethyl ester, polyacrylic acid amide or polyacrylic acid amides substituted at the nitrogen atom, such as polyacrylic acid-N-ethyl

amide, polyacrylic acid-N-diphenyl amide, polymethacrylic acid compounds, such as polymethacrylic acid methyl or polymethacrylic acid ethyl ester, the polymers of crotylidene cyanacetic acid esters, furthermore the caoutchouc like polymerisates of butadiene and isoprene. Instead of the above mentioned polymerisates of the vinyl compounds also interpolymers of these compounds with each other can be used. It may be mentioned that the polyvinyl ethers and interpolymers thereof are especially advantageous as components of the adhesives and coating materials of this invention.

The substances being solvents for the above mentioned polyvinyl compounds are known respectively may easily be ascertained by an expert by a simple test. The organic solvents suitable according to the present invention are given therewith. Also the substances being non-solvents for the above mentioned polyvinyl compounds are known or may easily be ascertained by a simple test. Substances being solvents for a certain polyvinyl compound may be of course non-solvents for another polyvinyl compound and vice versa.

The expression "non-solvent" is intended to comprise not only such substances as are not at all capable of dissolving the respective polyvinyl compound but also those substances which only bring about a slight dissolution or swelling of the polyvinyl compound.

As solvents and non-solvents, respectively, there may be mentioned, for instance, benzene, acetone, methyl ethyl ketone, furthermore ethanol, methanol, glycol, methyl glycol, ethyl glycol, diethyl ether, dibutyl ether, methyl acetate, ethyl acetate, methylene chloride, nitropropane, but also benzene, toluene, xylene, tetrahydrofuran or the like. Mixtures of these substances may, of course, also be used.

Advantageously such a quantity of the non-solvents is added to the solution of the polyvinyl compound that the precipitation of the polyvinyl compound just does not yet begin. This quantity depends on the kind of the single components of the material to be prepared according to this invention and on the use to which it is to be put and may easily be ascertained by an expert by a simple test. In some cases it may also be advantageous to use smaller quantities of the non-solvent.

The materials obtainable according to the present invention are especially suitable for such purposes as require a solid, flexible and elastic coating or agglutination. There come into considera-

tion the glueing together and the surface treatment of porous materials, such as leather, textiles, especially felt, card board, paper or the like. The usual additions, such as dyestuffs, pigments, resins and so on may also be applied.

The following examples illustrate the invention without being restricted thereto; the parts are by weight:

Example 1

20 parts of highly polymeric vinyl isobutyl ether are dissolved in 40 parts of benzine and 40 parts of acetone are added. A composition is obtained which when applied on porous materials, such as leather or textiles, slightly dried and pressed yields very solid agglutinations. The composition may also be used for preparing coatings, for example, on the materials mentioned before. For this purpose the composition, if de-

sired, may be incorporated with a pigment, for example 10% of iron oxide red pigment may be added.

Example 2

5 To a solution of 20 parts of highly polymeric polyvinyl isobutyl ether in 65 parts of benzine 15 parts of ethanol are added, whereby an adhesive of an action similar to that of example 1 is obtained.

Example 3

10 16 parts of an interpolymers of 80 parts of butadiene and 20 parts of acrylic nitrile are dissolved in 62 parts of methyl ethyl ketone and 22 parts of ethanol are added. A valuable adhesive is like-
15 wise obtained.

EUGEN BOCK.

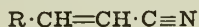
ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF
ACRYLIC ACID NITRILE DERIVATIVES

Peter Kurtz and Herbert Schwarz, Leverkusen-Wiesdorf, Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 12, 1941

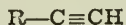
This invention relates to the preparation of acrylic acid nitrile derivatives of the formula



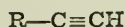
wherein R stands for an organic radical. The invention further pertains to the reaction involving the use of vinyl acetylene and hydrocyanic acid.

It has been disclosed in a copending application Ser. No. 343,269 filed June 29, 1940 that the reaction between acetylene and hydrocyanic acid under certain conditions yields acrylic acid nitrile. The process of the application mentioned above is based on the perception that catalysts for bringing about those addition reactions of acetylene which result in the formation of vinyl derivatives also effect the addition of hydrocyanic acid on acetylene. Briefly stated the process consists in bringing acetylene together with hydrocyanic acid into contact with an acid reacting solution of cuprous chloride as a catalyst.

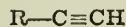
Now we have found that the effectiveness of the catalyst used in the process of application Ser. No. 343,269 is not limited to the addition of hydrocyanic acid on acetylene but is also effective in adding hydrocyanic acid on substitution products of acetylene of the formula



wherein R stands for an organic radical. Therefore our process consists in bringing substitution products of acetylene of the formula



wherein R stands for an organic radical together with hydrocyanic acid into contact with those catalysts as are used in the process of application Ser. No. 343,269. As derivatives of acetylene of the formula



there may be mentioned, for instance, vinylacetylene which yields 1-cyanbutadiene-1,3, when hydrocyanic acid is added thereto, according to the process of our invention.

As regards the catalyst it is to be pointed out that it may be composed in the same manner as stated in application Ser. No. 343,269. Thus,

for instance, an aqueous acid reacting catalyst may be employed, prepared from cuprous chloride and a salt of the class consisting of ammonium, amine and alkali salts. It is advantageous to add to the catalyst copper powder in order to maintain the copper salt in the monovalent state as cupric copper may cause undesired side reactions. The acid reaction of the catalyst is attained by adding a strong acid such as hydrochloric acid, hydrobromic acid, sulfuric acid or phosphoric acid and it is preferable to adjust the pH to at least 6.

A suited catalyst may be composed from 1100 parts of cuprous chloride, 590 parts of ammonium chloride, 950 parts of water and 29 parts of concentrated hydrochloric acid. Equivalents may be used for the chemicals named and the proportions of the constituents may be varied.

The reaction may be carried out at temperatures between 0-200° C but it is preferable to hold the temperature at about 60-80° C when working under atmospheric pressure. Obviously, the reaction may be carried out in a continuous process.

The following example illustrate our invention without, however, restricting it thereto, the parts being by weight.

Example

1100 parts of cuprous chloride and 590 parts of ammonium chloride are allowed to run into 950 parts of water while adding 30 parts of copper powder and 29 parts of concentrated hydrochloric acid and heated to 80° C with exclusion of air. The mixture is kept at this temperature for several hours. When cooled to room temperature 44 parts of vinylacetylene are added together with 40 parts of hydrocyanic acid, whereby the temperature of the mixture weakly rises. The mixture is stirred for 5 hours and then heated to 50° C for 10 hours and distilled off. The distillate consists of water and an oily layer which is separated from water, dried and distilled. 1-Cyanbutadiene-1,3 is obtained in a good yield, which distills at 56-60° C under a pressure of 44 mm.

PETER KURTZ.
HERBERT SCHWARZ.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR SEPARATION OF ACRYLIC ACID NITRILE

Peter Kurtz, Johannes Casper and Herbert
Schwarz, Leverkusen - Wiesdorf, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed February 12, 1941

Specification No. 343,269 describes a process of preparing acrylic acid nitrile which comprises bringing acetylene together with hydro-cyanic acid into contact with a suitable catalyst. This process is based on the perception that catalysts for bringing about those additional reactions of acetylene which result in vinyl derivatives thereof also effect the addition of hydro-cyanic acids on acetylene. The process consists in bringing acetylene together with hydrocyanic acid into contact with an acid reacting solution of cuprous chloride as a catalyst.

In this process acetaldehyde, monovinylacetylene, divinylacetylene, and higher boiling compounds are obtained as by-products which leave the reaction vessel together with the acrylic acid nitrile, the excess acetylene, the nonconverted hydrocyanic acid, and water vapours. The separation of the acrylic acid nitrile may be accomplished by condensing it together with the by-products—with the exception of acetylene which is recycled—and fractionally distilling. The separation of acrylic acid nitrile from monovinyl acetylene, acetaldehyd, and hydrocyanic acid causes no difficulties and with respect to those by-products a fractionation would be operable. Difficulties however arise from the divinyl acetylene due to the similar boiling points of this substance and acrylic acid nitrile and practically speaking separation from divinyl acetylene is impossible by a distilling operation. A further difficulty consists in the sensitiveness of divinyl acetylene against heat and therefore a heating process must be avoided.

Now we have found that the acrylic acid nitrile may be separated in a simple manner from the reaction mixture obtained according to the process of specification 343,269. Our process consists in a washing operation of the reaction mixture with a suited solvent especially water.

The gas mixture leaving the reaction vessel is continuously washed in a washing column preferably under atmospheric pressure and at low temperatures (0–20°C). Only small quantities of acetylene and monovinyl acetylene but almost the total quantity of acetaldehyd, hydrocyanic acid and acrylic acid nitrile dissolve in the washing medium. By using for example for the washing

of volume of water of a temperature of 15–20°, 96% of the acrylic acid nitrile are absorbed, the water containing only 0.4% of dissolved acetylene and traces of monovinylacetylene. Divinyl acetylene is not dissolved in the washing water. The loss of acetylene which takes place in the washing process, is therefore very low, what is especially to be pointed out. By increasing the ratio gas mixture to washing water it is possible to wash out the acrylic acid nitrile in a still more complete way but then the quantity of the dissolved acetylene is also increased. Generally speaking all conditions must be chosen in such a way that a high yield of dissolved acrylic acid nitrile corresponds to a small loss of acetylene only. If necessary however it is possible to recover and recycle the acetylene dissolved in the washing water.

The aqueous solution obtained is distilled in order to get the acrylic acid nitrile.

The acetylene which leaves the washing column contains mono- and divinyl acetylene. It may be freed from these products by low cooling and recycled.

Example

Through 2.5 liters of a catalyzer composed of 300 parts of cuprous chloride, 100 parts of ammonium chloride, 5 parts of concentrated hydrochloride acid, 10 parts of copper powder and 400 parts of water, 0.25 liters of acetylene together with 26 g of hydrocyanic acid per hour are passed in at a temperature of 80° C. The escaping gas mixture is washed in a usual washing column filled with Raschig-rings with 2 liters of water per hour. The aqueous solution leaving the column is continuously distilled. An azeotropic mixture consisting of acrylic acid nitrile and water passes over which is somewhat contaminated with hydrocyanic acid and acetaldehyd. The raw acrylic acid nitrile which forms an oily layer is separated, dried, for example with calcium chloride and then fractionated. After a small fraction at a low temperature which consists chiefly of acetaldehyd and hydrocyanic acid the pure acrylic acid nitrile distills at 76–78°C (760 mm).

PETER KURTZ.
JOHANNES CASPER.
HERBERT SCHWARZ.

ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING LACTAMS

Otto Drossbach, Heinrich Hopff, and Karl Huttner, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 13, 1941

The present invention relates to an improved method of producing lactams.

Lactams are usually produced by converting cyclic ketones into their oximes and subjecting the oximes to the Beckmann rearrangement. This last-named operation is difficult to perform when carried out on a large scale, since the rearrangement proceeds with violence and tends to give rise to overheating or even explosions.

We have now found that lactams can be produced in a one-stage process by passing vaporized dicarboxylic acids, the chain length of which allows of the formation of lactams, i.e. which contain at least 4, with preference 6 or more carbon atoms in the molecule together with ammonia and hydrogen at an elevated temperature over catalysts exerting a hydrogenating and dehydrating action. Catalysts of the said kind are those containing the usual hydrogenation catalysts, such as nickel, cobalt and copper as the hydrogenating constituent and the usual dehydration catalysts, such as phosphoric acid or boric acid as the dehydrating constituent. Both constituents are employed in sufficient quantities so that both the hydrogenation and the dehydration will proceed to the desired extent. Generally the constituents, i.e. for example nickel and phosphoric acid, are employed in approximately equivalent quantities, but it is usually of advantage to employ the hydrogenating component in a certain excess over the dehydrating component. Using the dehydrating component, for example phosphoric acid, in excess, would favor the formation of nitriles and amides. It is not advisable to use catalysts exerting an alkaline reaction. The catalysts may be used on carriers, for example on pumice stone or silica gel, or in admixture with inert substances.

Dicarboxylic acids suitable in the present reaction are, for example, glutaric acid, pimelic acid and especially adipic acid. The dicarboxylic acids may also be employed in the form of their anhydrides. The treatment may be carried out, generally speaking, at temperatures between 100 and 350°C; it is, however, advisable to work at the lowest possible temperature within said range and not to heat over 300°C. Temperatures ranging from 150 to 260°C have proved most suitable for the purpose.

The process can be carried out under ordinary pressure, but under increased or reduced pressure as well. The time of reaction is adjusted in dependence on the catalyst, the temperature and the acid employed, so that undesired side-reactions which are liable to occur when too

short or too long a stay in the catalyst chamber is chosen are avoided as far as ever possible.

In the presence of hydrogen and ammonia dicarboxylic acids are capable of undergoing most different conversions and kinds of decomposition. The number of reaction products imaginable is very large, depending on whether one or both carboxylic groups are reduced or converted into the nitrile group and then reduced, whether carbon dioxide is split off etc. It is therefore surprising that the reaction can be caused to proceed preponderatingly in the desired direction so that the industrially important lactams can be obtained from dicarboxylic acids in one operation.

The following examples serve to illustrate how the present invention may be carried out in practice but the invention is not restricted to these examples. The parts are by weight.

Example 1

100 parts per hour of adipic acid are quickly evaporated and passed together with 155 parts of ammonia and 9 parts of hydrogen at from 200 to 220°C over 375 parts of a nickel phosphate catalyst obtained by mixing 4.5 kilograms of nickel carbonate, 1.2 kilograms of phosphoric acid, 3 kilograms of water and 30 liters of pea-sized pumice stone, evaporating the mass to dryness while stirring and reducing it with hydrogen at 350°C. The mixture leaving the reaction vessel is cooled and washed with water. ϵ -Caprolactam is obtained besides some ϵ -aminocapronitrile and small quantities of diamines. The lactam can be obtained in a pure state by distillation under reduced pressure.

Instead of the above-mentioned catalyst a catalyst may be employed which has been prepared in an analogous manner from 5 kilograms of nickel carbonate, 5 kilograms of cobalt carbonate, 3 kilograms of phosphoric acid and 100 liters of pumice stone, the catalyst having been reduced for 9 hours. By passing at from 210 to 220°C over each liter of the said catalyst per hour a mixture of 120 liters of hydrogen, 180 liters of ammonia containing in each cubic meter 67 grams of adipic acid vapor, caprolactam is likewise obtained in a good yield besides adipic acid dinitrile.

Example 2

A mixture of 100 liters of ammonia, 50 liters of hydrogen and 23 grams of vaporized adipic acid is passed per hour over 1 liter of the nickel phosphate catalyst referred to in Example 1 at 250°C. When the reaction mixture is cooled solid ϵ -caprolactam separates out first. On further

cooling a liquid reaction product is condensed which separates into oily constituents and water formed in the reaction. The oil is distilled under reduced pressure whereby the caprolactam is separated from any by-products formed, such as aminocapronitrile and hexamethylene imine.

Example 3

80 liters of hydrogen heated to 180°C are hourly passed through molten glutaric acid heated to the same temperature. The current of hydrogen charged with glutaric acid vapor is united with 40 liters of ammonia per hour, heated to 300°C. This combined gas-vapor current is passed over 1 liter of a nickel phosphate catalyst precipitated on pumice stone which has been heated to 285°C. The mixture leaving the chamber in which the catalytic reaction goes on is cooled and the condensed lemon-yellow oil is distilled in vacuo. δ -Valerolactam is thus obtained in a yield of 55 per cent of the theory. It boils at 108°C under a pressure of 5 millimeters (mercury gauge) and melts at 40°C.

The said catalyst is prepared by dissolving 22.5 kilograms of secondary ammonium phosphate in 150 liters of hot distilled water and adding 66.7 kilograms of nickel carbonate while stirring. After adding 1000 liters of granular pumice stone (with grains of about 6 millimeters diameter) the mass is dried on the water-bath while stirring intensely. The dried catalyst is reduced with hydrogen at 350°C for 24 hours.

The catalyst thus obtained is also suitable for use in converting succinic acid in a similar manner as disclosed above into γ -butyrolactam (melting at 25°C and boiling at 105°C under a pressure

of 5 millimeters (mercury gauge)); in order to obtain as complete as possible a conversion of the succinic acid care should be taken that the reaction mixture remains for a sufficient time in the reaction space.

Example 4

A mixture of 20 liters of ammonia and 100 liters of hydrogen which is charged with 4 grams of the vapors of adipic acid and which is heated to 290°C is passed per hour at 285°C over 1 liter of a nickel-boric acid-phosphoric acid catalyst.

On cooling the reaction mixture, a clear yellowish oil is condensed which is subjected to distillation under reduced pressure. After removing therefrom slight amounts of water, a fraction consisting of the azeotropic mixture of hexamethyleneimine and water is obtained first, whereupon ϵ -caprolactam of high purity is distilled over at 120°C under a pressure of 5 millimeters (mercury gauge); the lactam crystallizes on further cooling and without being further purified has a melting point of 68°C. The yield of hexamethyleneimine amounts to 18 per cent, while that of ϵ -caprolactam amounts to 45 per cent of the theory.

The said catalyst is prepared by pasting 102 grams of 100 per cent boric acid, 189 grams of 100 per cent phosphoric acid and 665 grams of nickel carbonate with water, mixing the paste with 10 liters of granular pumice stone, drying the mass and treating it with hydrogen at 350°C.

OTTO DROSSBACH.
HEINRICH HOPFF.
KARL HUTTNER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE REMOVAL OF NOXIOUS METAL COMPOUNDS FROM RUBBER OR SUBSTANCES SIMILAR TO RUBBER, AND FROM DISPERSIONS THEREOF

Godfried Johan van der Bie, Buitenzorg, Java, Netherlands East Indies; vested in the Alien Property Custodian

No Drawing. Application filed February 14, 1941

It is well known that minute quantities of certain metal compounds, such as copper, manganese, or iron salts, deleteriously affect the durability of crude or vulcanized rubber. In actual practice, therefore, limits have been fixed for the quantity to be tolerated of any such metals.

Furthermore it is known that minute quantities of the abovementioned metal compounds are present also in rubber dispersions. Certain kinds of latex, when freshly collected, already have a fairly large copper content. The metal compounds present in latex are usually in part dissolved, and in part they are in a non-dissolved state, that is to say that they are adsorbed to the rubber particles, dispersed in the serum, or precipitated onto or in the rubber particles. The aim of the invention is to cause the noxious insoluble metal compounds to become soluble, and to remove the same.

Upon coagulation, about half of the metal compounds present remain in the serum, the remainder being left in the rubber.

The metal compounds, more specifically the copper compounds, have a deleterious effect upon the ageing properties of rubber, though this noxious influence is partly counteracted again by the so-called anti-oxidants, substances occurring in natural latex, and which protect it against depolymerisation or oxidation. If, however, one has to deal with purified rubber, such as is used for electrical purposes for example, then the anti-oxidants have as a rule been removed, so that the noxious influences of these metal compounds become increasingly noticeable.

In purifying rubber dispersions through hydrolysing the non-rubber components, as for example through heating with caustic potash, the metal compounds are decomposed in the course of the hydrolysis and almost entirely converted into compounds which, upon the coagulation of the latex, form insoluble compounds, so that a considerable proportion of the metals, such as the copper referred to, is retained in the purified rubber. Presumably the copper precipitates in the shape of sulphuretted compounds. Through hydrolysis sulphide ions are produced by the non-rubber components.

To enhance the durability of rubber it is of importance to obtain a product with a low content of noxious metals, more specifically a low copper content. Thus it is desirable to endeavour to decrease the metal content of rubber, and obviously more specifically that of rubber varieties with a high metal content. The high metal content of rubber may be due to a variety of causes,

for example to the high metal content of crude latex, or to contamination in the course of the preliminary treatment of the latex. Synthetic dispersions as a rule contain noxious metal compounds derived from the factory plant.

Dissolved metal compounds may be removed, together with the serum components, by means of creaming, centrifuging, or other known processes. The coarser particles of metal compounds that may be present in the serum, can be removed through clarification.

Now the invention refers to a process by means of which the metal compounds, and more specifically the copper compounds present in the latex or in the rubber particles in an insoluble state, can be converted into soluble compounds, thereupon to be removed by the methods known in connection with the removal of soluble compounds present in rubber dispersions.

According to the invention the dissolving of metal compounds is effected by converting them into soluble complex compounds, and by thereupon removing the compounds thus made soluble, as for example through dialysis, creaming, centrifuging, adsorption, or in any other known way.

A very suitable method of converting metal compounds into soluble complex compounds is by treating the rubber dispersion with a cyanide.

Copper compounds can also be converted into ammonia or hydroxyl complexes, provided no sulphide ions be present in the liquid.

The dissolving of insoluble metal compounds can also be effected simultaneously with other processes, for example at the same time that hydrolysis is taking place, as in the case of a treatment with caustic potash, or when some other purifying treatment is being applied.

The dissolving of a noxious metal present in a rubber dispersion will in actual practice have to be effected in an alkaline medium, in view of the stability conditions of the rubber dispersion. Also the removal of the metal complexes will have to be effected in an alkaline medium, that is to say, therefore, prior to coagulation, which usually is effected in an acid medium.

Through a process such as is indicated above, it may be possible to reduce, for instance, the copper content of rubber to one fourth of the original amount present.

The quantity of cyanide to be applied is preferably to be kept as small as possible. Experiments have shown that very minute quantities, say 30 mg per litre, already suffice to reduce the copper content quite considerably. Thus it was

found, for example, that the copper content per 100 g of rubber had been reduced from 0.86 mg to 0.51 mg. In actual practice quantities of from 0.1–0.2 g of cyanide per litre are to be recommended. By adding this quantity a reduction, for example, from 0.86 mg to 0.23 mg of copper per 100 g of rubber is effected.

Through heating the dispersion, after cyanide has been added, the solution of the metals, such as that of copper, is promoted, whilst it also makes it possible to use only small quantities of cyanide. If the dispersion is not heated, then it will be necessary to apply a larger quantity of cyanide for a reduction of the metal content down to 0.2–0.25 mg of copper per 100 g of rubber.

Copper that has been made soluble can be removed, along with other serum substances, in various ways, such as through centrifuging, creaming, dialysing, adsorption, ultra-filtration, etc. Its removal through creaming with konnyaku meal is particularly suitable, seeing that this makes it possible to effect a very marked decline in the copper content of the final rubber product.

It is probable that copper is adsorbed onto the konnyaku meal, and that this causes the considerable decline in the copper content.

GODFRIED JOHAN VAN DER BIE.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PREPARING SULPHUR DYES SOLUBLE IN WATER

Filippo Bovini, Milan, Italy; vested in the Alien
Property Custodian

No Drawing. Application filed February 18, 1941

It is known since a long time, that many sulphur dyes obtained by precipitating the respective molten masses with acids or air, show a tendency to dissolve under the action of sulphite or sodium bisulphite.

The compounds obtained by salting or evaporating sulphite or bisulphite solutions show a certain solubility in water and they do not reprecipitate from their diluted aqueous solutions under the action of acids or by oxidation with air.

Laval's cachou was among the first sulphur dyes treated according to the above procedure, followed later on by other sulphur browns obtained by the combination of a variety of intermediates with sulphur or polysulphides.

The constitution of these soluble compounds, which has been differently explained, is insignificant as far as the practical purpose of this invention is concerned, namely dyeing and printing textile fibres, leather dyeing and similar operations.

As a matter of fact, these compounds have been experienced in the respective fields of application, especially in cotton and wool dyeing, but in spite of certain developments directed to improve their tinctorial properties, results have shown unsatisfactory.

When dyed on wool in acid solution they show very scarce tinctorial properties, and when applied to cotton they show even in the presence of sodium sulphide or of other reducing agents less affinity and much lower covering power than the sulphur dyes they derive from.

In leather dyeing the properties of these compounds appear to be somewhat better, but here too no remarkable progress has even been reached.

Therefore, although the discovery of these soluble compounds obtained from brown sulphur dyes by treatment with sulphite or bisulphite is far behind us, they have been completely abandoned.

One cause of the lack of success is certainly due to the unsatisfactory processes proposed for their preparation.

In fact, when preparing sulphur browns according to the patents covering the different processes, it is found that many dyestuffs do not dissolve at all and others only partially and, in any case, it is then difficult, and sometimes impossible, to separate products in powder being completely soluble in water, of valuable tinctorial properties and suitable for practical application.

It may be said, therefore, that no reference is found in literature about a process for the manu-

facture of soluble sulphur browns in form meeting trade requirements.

I have now found that it is possible to obtain compounds completely soluble in water in form of a highly concentrated fine powder having excellent tinctorial properties and the fastness required by treating orange, brown or olive sulphur dyes with sodium bisulphite solutions.

Heat treatment is preferred, either of the finished dyestuff or of the material during an intermediate working step, namely, treating (a) the raw powder obtained by melting various intermediates with sulphur; (b) the paste obtained after precipitating the above raw powder by acid or air from the solution in sulphide; (c) the paste obtained by precipitating, at various temperatures the aqueous solutions of melting products by acid or air, on certain intermediates by sulphides or polysulphides, or the bisulphitation products by acids or salt, according to the examples stated above.

The compounds obtained are of different solubility and more or less sensible to the action of salts and to room pH, according to their nature. Many of them are insoluble or almost insoluble in the bisulphitic room in which they are formed, while they are readily soluble in water after drying and at a suitable degree of dilution.

Also the stability of these compounds to the hydrolytic action of water varies according to the nature of the product, to the temperature, and to the action being on free acid or on sodium salts.

This process is of general character and there are few sulphur browns which do not give good results by this treatment. It can be applied to sulphur browns derived from intermediates of various nature obtainable by different methods of sulphuration, as it appears from the examples given hereafter.

The soluble compounds in question are used in dyeing in the presence of sodium sulphide, hydrosulphide or other suitable reducing agents, and they generally possess a good tinctorial property and a fair affinity also in cotton dyeing. But in view of their affinity, covering power and fastness they are particularly suitable for dyeing regenerated cellulose fibres, casein wool, leather, and for Vigoureux-printing on a large variety of fibres.

Examples 1.—The melting mass of Bright Sulphur Orange R (Schultz Tab. VII 1063) is dissolved in a solution of sodium sulphide and reprecipitated by acidification. The paste obtained is kneaded with the double weight of sodium bi-

sulphite in solution of 35° Bé, heated up to 90° C. and maintained at this temperature during about 2 hours. It is then diluted, allowed to cool and filtered. The precipitate is mixed with small amounts of sodium carbonate and dried.

The dry powder thus obtained is completely soluble in water and in the presence of reducing agents it is suitable for dyeing, cotton, viscose, casein wool (Lanital) and leather in bright orange-brown shades of excellent fastness.

Examples 2.—The raw mass obtained by melting m-toluylene-diamine with polysulphides is dissolved in hot water, filtered and precipitated by acids in the ordinary way. The paste thus obtained is thoroughly mixed with a double amount by weight of bisulphite in solution of 35° Bé, and then heated up to 90° C. and maintained at this temperature for an hour. The mass is then diluted with hot water in such a way that the product passes entirely in solution. It is filtered slightly salted and the dyestuff is precipitated by hydrogen chloride. Small amounts of sodium carbonate are added to the filtered paste and the product is dried in the usual way.

The powder thus obtained dissolves completely in water and in the presence of sulphur, hydrosulphite, etc. it dyes cotton, viscose, casein wool (Lanital) and leather, in yellowish cachou shades of excellent fastness.

Examples 3.—Sulphur Brown 6 R (ACNA) in form of powder is kneaded with a fourfold amount by weight of bisulphite in solution of 35 Bé, diluted with water and slowly heated up to 90°C. The material is then filtered, salted and completely precipitated by hydrogen chloride. It is filtered and the paste obtained is dried with a small amount of sodium carbonate.

The dry powder thus obtained is completely soluble in water and in the presence of sulphur, hydrosulphite, etc. it dyes cotton, viscose, casein wool (Lanital) and leather in brown-red shades.

Examples 4.—The dry dyestuff obtained by melting 2-4-dinitroaniline and polysulphides is thoroughly mixed with an eightfold amount by weight of sodium bisulphite solution of 35° Bé, heated up to 60°C and diluted with an equal amount of water. It is filtered, salted, and hydrogen chloride is added until the precipitation is completed. The paste obtained by filtration is mixed with small amounts of sodium carbonate and dried.

The dry dyestuff powder is entirely soluble in water and in the presence of sulphur, hydrosulphite or other suitable reducing agents it dyes cotton, viscose, casein wool (Lanital) and leather in brown-black shades of excellent fastness.

Examples 5.—The raw melting mass of Green Sulpholive B (ACNA) in finely pulverized form is mixed with a tenfold amount by weight of sodium bisulphite in solution of 35° Bé, heated up to 95°C and maintained at this temperature until the product is completely dissolved. It is diluted, filtered and salted. It is allowed to cool at room temperature and precipitated by the necessary amount of hydrogen chloride. It is filtered and the paste thus obtained is dried after an addition of small amounts of sodium carbonate.

The powder of this dyestuff is completely soluble in water, and in the presence of sulphur, hydrosulphite or other reducing agents it dyes cotton, viscose, casein wool (Lanital) and leather in green-olive shades of good fastness.

FILIPPO BOVINI.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PRODUCING CONDENSATION PRODUCTS

Winfried Hentrich, Rodleben B. Dessau-Rosslau,
and Erik Schirm, Dessau, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed February 19, 1941

This invention relates to a process for producing condensation products having at least three acyl sulfamide groups in the molecule. More particularly it relates to the production of tanning principles having at least three acyl sulfamide groups in the molecule by condensing organic acyl halogenides with organic sulfamides.

The principle object of this invention is to provide industry, particularly the leather and textile industry with an effective class of tanning principles for tanning purposes for reserving wool and for making colorlakes.

It has been found that valuable condensation products are obtained by producing acyl sulfamides containing no less than three acyl sulfamide groups in the molecule, in converting the halogenides or anhydrides of organic sulfonic acids or carboxylic acids with aromatic sulfamides, having sulfamide groups non-substituted at the nitrogen, in the presence of alkaline agents.

Such condensation products are obtained in a simple way by (a) the condensation of one mol of a tri- or tetrasulfochloride with three or four mols respectively of a monosulfamide and (b) the condensation of one mol of a tri- or tetrasulfamide with three or four mols respectively of a monosulfochloride. But one may also condense e. g. one mol of a disulfonic chloride with one mol of a disulfamide or two mols of a trisulfochloride with three mols of a disulfoamide or vice versa three mols of a disulfochloride with two mols of a trisulfamide and so on. In the latter cases high molecular condensation products are obtained with an indefinite number of disulfimide groups.

Among the sulfochlorides applicable according to the present invention are named e. g. benzene-sulfochloride, benzene-1,3-disulfochloride, p-toluenesulfochloride, toluene-2,4-disulfochloride, p-chlorobenzenesulfochloride, chlorobenzene-2,4-disulfochloride, m-nitrobenzene-sulfochloride, phenol-2,4,6-trisulfochloride, benzoic acid-m-sulfochloride, salicylic acid-sulfochloride, the various di- and tri-sulfochlorides of the naphthalene, naphthalene-1,3,5,7-tetrasulfochloride, pyrene-3,5,8,10-tetrasulfochloride, carbazol-tetrasulfochloride, the sulfochlorides of the diphenyl and the like. As carboxylic acid derivatives there are to be considered e. g. acetic acid anhydride, acetyl bromide and the chlorides of the higher fatty acids, phosgene, oxalyl chloride, adipic acid chloride, benzoyl chloride, iso- and terephthaloyl chloride etc.

As sulfamides one may apply e. g. all the sulfamides obtainable from the aforementioned sulfochlorides by means of ammonia. In certain cases

it is unnecessary to isolate the sulfamides i. e. if poly sulfochlorides are used as initial materials. One may simply cause the reaction of same upon ammonia observing, however, that for one sulfochloride group there is present less than one mol of ammonia, and in this way also high molecular condensation products are obtained with an indefinite number of disulfimide groups, eventually besides sulfamide groups i. e. when for two sulfochloride groups more than one mol of ammonia was applied. The sulfamides may also contain amino groups besides the substituents that are possible with the halogenides or anhydrides of the sulfonic and carboxylic acids, such as alkyl, halo-, hydroxy, alkoxy and nitro groups. In this case at the condensation also acyl amide groups are formed besides the acyl sulfamide groups which are able of improving advantageously the properties of the condensation products.

A further manner of carrying out the present process consists in taking N-acyl-sulfamides which contain besides the imide hydrogen at least one exchangeable hydrogen atom linked to O, N or S, and in condensing same with organic compounds possessing reactive halogen atoms, whereat the components are to be selected in such a manner that the obtained condensation products contain no less than three acyl sulfamide groups.

As acyl sulfamides of the aforementioned kind are to be named e. g. the m,m'-dihydroxy-dibenzene-disulfimide, the p-mercaptol-benzene-p'-toluene-disulfimide, the N-(p'-aminobenzene-sulfonyl)-benzamide, the N-(m'-aminobenzoyl)-p-toluene-sulfamide, the m,m'-diaminodibenzene-disulfimide. The compounds to be applied as second components with reactive halogen atoms may be characterised by the following examples: sulfochlorides, either mono- or poly-sulfochlorides of the aromatic series, chlorides of mono- and poly-carboxylic acids such as benzoyl chloride, phosgene, adipic acid chloride, isophthaloyl chloride, further halogen-methyl compounds, such as benzyl chloride, menaphthyl chloride, o-, m- or p-xylylene-dibromide, 4,6-di-(chloromethyl)-1,3-xylyl or 2,4-di-(chloromethyl)-anisol, further aromatic compounds halogenated in the nucleus with reactive halogen atoms, such as the 2,4-dinitrochlorobenzene, the 1,3-dinitro-2,4,5-trichlorobenzene, finally heterocyclic compounds with the grouping



preferably twice or three times in the molecule such as 2,4-dichloropyrimidine, 2,4-dichloroquinazoline or cyanuric chloride.

It has been found that when in the afore-described processes in first and/or second place components are applied containing or forming monoaryl substituted sulfamide groups it is unnecessary that the condensation products contain at least three acyl sulfamide groups. The number of the acyl sulfamide groups may in those cases even be only two or one as far as the sum of the acyl sulfamide and sulfamide groups is no less than three.

The components employed in first and/or second place may contain watersoluble rendering groups such as the sulfonic acid, sulfuric acid ester, carboxylic, polyglycol ether, quaternary ammonium groups etc.

The products made according to the present invention are able to transform animal hides into leather and are valuable tanning principles. They may also be used as reserving agents for wool against the dyeing with direct cotton dyestuffs and for making colorlakes by the conversion with basic dyestuffs.

Example 1

513 parts by weight of p-toluol-sulfamide are dissolved while adding 130 parts by weight of sodium hydroxide in 2500 parts of water. To this solution at room temperature 424 parts by weight of naphthalene-1,3,5-trisulfochloride are added which are stirred together with 200 parts of water to form a fine paste; then the mixture is stirred at 25 to 30°C, and as soon as the alkaline reaction diminishes soda lye is added so that the mixture remains constantly alkaline to phenolphthaleine. If at the temperature mentioned the conversion begins to cease the mixture is warmed up at first to 50°C and, if the reaction does not advance, one continues warming up to 90–95°C and keep this temperature until the reaction remains alkaline for ½ to 1 hour, which indicates the end of the conversion. Then the mixture is cooled down to 60°C, common salt and hydrochloric acid for acidifying are added, till Congo paper dyes blue, whereupon one continues cooling down to room-temperature and filters off the resinous amorphous condensation product. It dissolves easily in hot water and the solution standardized to a pH-value of 3 to 4.5, may now immediately be employed for tanning purposes.

Example 2

444 parts by weight of naphthalene-1,3,5,7-tetrasulfamide are suspended in 3000 parts of water and dissolved by an addition of 170 parts by weight of sodium hydroxide. Then 1100 parts by weight of 3,4-dichlorobenzene-sulfochloride, pasted with water, are introduced into the said solution at room temperature. By a gradual addition of soda lye and an increasing of the temperature the condensation is performed quite similarly as described in example 1). Also the isolating of the condensation product from the ready made reaction mixture can be done to the method shown in example 1) and the result is also an easily watersoluble resin with tanning properties.

Instead of the 3,4-dichlorobenzene-sulfochloride one may likewise employ the equivalent amount of benzoyl chloride. In this case the method distinguishes itself from the indicated one merely by the fact that the condensation is begun at temperatures near to the ice-point and only after an addition of the whole amount of benzoyl-chloride it is slowly warmed up.

Example 3

331 parts by weight of phenol-2,5,6-trisulfamide are dissolved while adding 130 parts by weight of sodium hydroxide in 2000 parts of water. 435 parts by weight of toluene-2,4-disulfochloride are finely ground with water and the paste is added to the above solution at room temperature. Then one proceeds exactly as described in the examples 1 and 2 and obtains likewise a resinous tanning substance but of an indefinite, high molecular weight.

If less than 435 parts by weight of toluene-disulfochloride—e. g. 290 parts by weight only—for 331 parts by weight of phenol trisulfamide are used, similar high molecular bodies are obtained which, however, besides the disulfimide groups contain also free sulfamide groups and form also good tanning principles.

Example 4

365 parts by weight of naphthalene-1,3,6-trisulfamide are dissolved in 2000 parts of water while adding 130 parts by weight of sodium hydroxide. Into this solution phosgene is introduced at 10 to 20°C, till an increase of weight by 100 parts by weight is attained. During the introduction the reaction of the solution is kept permanently alkaline by a gradual addition of soda lye. Then for some time the mixture is warmed up to 50°C, is acidified and separated out by salt. The precipitation is filtered in the cold and dried. The thus obtained resin in its high molecular structure resembles the product of the preceding example. It is a very good tanning principle. The amount of the applied phosgene may be increased up to about 150 parts.

Instead of phosgene one may likewise apply, with the same satisfactory result, the equal weight amount of chlorocarbonic acid-trichloromethyl ester.

Example 5

424 parts by weight of a technical mixture of the naphthalene-trisulfochloride-1,3,6 and -1,3,7 are pasted with water and the paste is stirred, at about 0 to 5°C, into a solution of 80 parts by weight of ammonium chloride in 800 parts of water. Then slowly and at the same temperature, 60 parts by weight of sodium hydroxide are introduced in the form of a 30%-solution, whereupon stirring is continued for one hour at 0 to 5°C. Now the temperature is raised up to 20°C and a further amount of soda lye is added, as soon as the phenolphthaleine alkaline reaction disappears and the condensation is accomplished exactly as described in example 1). The working up of the precipitation is done as per example 1) and it results a tanning substance which according to its constitution resembles the product obtained as per example 3).

If in this example an increasing amount of ammonium chloride up to appr. 107 parts by weight is used, high molecular products are obtained which besides the disulfimide groups contain non-substituted sulfamide groups to an enhanced extent (see example 3, 2nd paragraph).

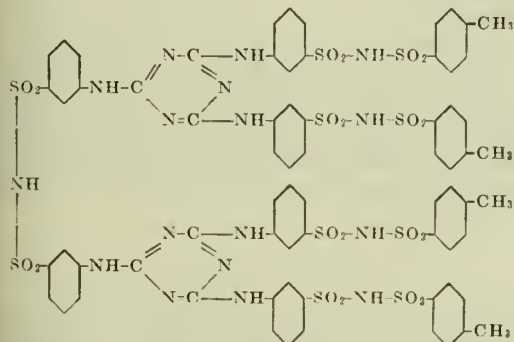
Example 6

326 parts by weight of m-amino-benzene-p'-toluene-disulfimide (made by condensation of m-nitrobenzene-sulfochloride with p-toluene-sulfamide in the presence of soda lye, and reduction of the nitro group) are dissolved while adding 40 parts by weight of sodium hydroxide in 2000 parts of hot water and the solution is cooled down

to 2° while well stirring; during this process the sodium salt of the disulfimide crystallises out partly. Into this suspension, at 2 to 5°C a solution of 65 parts by weight of cyanuric chloride in 250 parts by volume of acetone is stirred in, or the cyanuric chloride is immediately introduced in a finely pulverized form. One continues with stirring at 2 to 5°C for one hour, whereupon the liquid is carefully neutralised with sodium bicarbonate, till Congo-paper is dyed but just blackish, then the temperature is raised to 20°C and one continues adding sodium bicarbonate as soon as the liquid begins to turn Congo acid; but at the same time one takes care that there remains a distinctly litmus-acid reaction. As soon as at room temperature the splitting off of acid ceases, one warms up to 40–50°C whereat a clear solution is obtained and at this temperature by a careful addition of sodium bicarbonate a constantly litmus-neutral reaction is formed. Then the mixture is warmed up to 90–95°C and is stirred at this temperature for one hour, whereupon so much soda is slowly added that the solution remains finally slightly litmus-alkaline. Then one cools down to 50°C, acidifies with hydrochloric acid till Congo-paper is dyed blue, whereupon the cooling down to room temperature is continued; now the precipitated and still plastic resin is separated from acid water and dried at 100°C. The output is quantitative. The reddish powder obtained after the puerizing of the dry substance dissolves easily in water with a strongly acid reaction. The solution shows tanning properties.

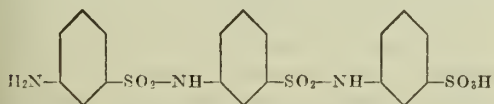
Example 7

At first one proceeds exactly as in the preceding example, but increases the amount of the cyanuric chloride up to 98 parts by weight. After a constantly litmus-neutral reaction is attained at 40 to 50°C, a solution of 82 parts by weight of m,m'-diamino-dibenzene-disulfimide and 10 parts by weight of sodium hydroxide in 250 parts of water are added and the temperature is increased to 90°C. The further process is exactly as before. The obtained condensation product distinguishes itself externally scarcely from that of Example 6. Its constitution formula is as follows:



Example 8

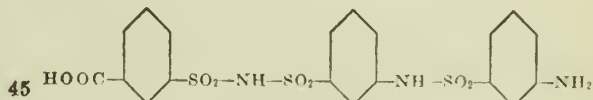
483 parts by weight of metanilyl-metanilyl-metanilic acid of the formula



are dissolved while adding 40 parts by weight of sodium hydroxide in 2000 parts of water. On the other hand a solution of 98 parts by weight

of cyanuric chloride in 400 parts by volume of acetone are introduced, while energetically stirring, into 1300 parts of iced water. To the thus obtained suspension the above amino-acid-solution is slowly added without exceeding the temperature of 5°C. During this addition the suspension is transformed into a clear solution. One continues stirring for one hour at ice-temperature, then warms up to 20°C and keeps this temperature also for one hour. Now sodium bicarbonate is carefully added, until Congo-paper will be dyed but blackish and this reaction is maintained for a further hour. Then one warms up to 40–50°C and by a further addition of bicarbonate one makes up to constant Congo-neutral till litmus-acid. By means of a diazotizing-test one determines that no remarkable amounts of unbound amino acid are present in the solution, then one adds a solution of 82 parts by weight of m,m'-diamino-dibenzene-disulfimide made according to Example 7, whereupon the mixture is warmed up to 90–95°C. At this temperature a constant slightly litmus-alkaline reaction after one hour's stirring by an addition of soda is made. As soon as a diazotising-test indicates the end of the conversion the mixture is cooled down to 60°C is made strongly Congo-acid by addition of hydrochloric acid and is cooled down to room temperature. The resin precipitated in the warmth as plastic mass solidifies, is puerized, sharply sucked off and dried at 100°C; the output is quantitative. The thus obtained reddish powder is an excellent individual tanning substance and supplies a white, well filled flexible leather of a great fastness to light and a resistance to tearing.

A similarly valuable tanning substance is obtained, if instead of the metanilyl-metanilyl-metanilic acid one takes the N-metanilyl-metanilyl-benzoic acid-m-sulfamide of the formula



and performs for the rest the condensation exactly in the afore-described manner.

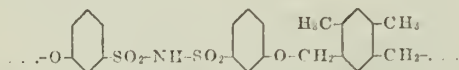
Example 9

424 parts by weight of naphthalene-1,3,5-trisulfochloride are ground with water to form a fine paste, which is introduced at room temperature into a solution of 524 parts by weight of the dry sodium salt of the m,m'-diamino-dibenzene-disulfimide in 2500 parts of water. After some stirring the mixture turned acid is neutralized with soda lye; then, as soon as the separation of acid diminishes, the temperature is raised gradually and finally up to 90–95°C, and by a careful addition of soda lye or soda the reaction is maintained litmus-neutral as far as possible. Finally one renders slightly litmus-alkaline and, if this reaction lasts for 1/2 to 1 hour without a further alkali-addition, the mixture is made strongly Congo-acid with hydrochloric acid after cooling down to about 60°C. The further working up is done as per example 1. In this case in approximately a quantitative output a resinous condensation product of excellent tanning-properties is obtained.

Example 10

69 parts by weight of sodium are dissolved in 2000 parts by weight of tetrahydrofurfuryl alcohol (or glycol-monoethyl ether). To this solu-

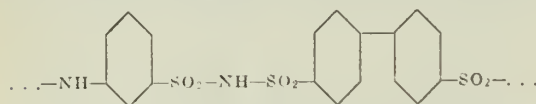
tion 329 parts by weight of m,m'-dioxydibenzene-disulfimide (obtained from the corresponding diamino-compound by tetrazotising and warming of the aqueous bis-diazonium-salt solution) are added, then the mixture is warmed up, whereby the imide dissolves while forming the trisodium compound. The solution is now cooled down to room temperature and a solution of 203 parts by weight of 4,6-dichloro-methyl-1,3-xylol is stirred in. By warming up on the water bath the conversion is finished. Now the organic solvent is distilled off under a strongly diminished pressure and the residue is taken in water. From the aqueous solution the high molecular condensation product, the "structure element" of which is



is precipitated as resin when acidifying with mineral acids. The precipitate is soluble in water and possesses tanning properties; the neutralised solution supplies colorlakes with the salt solutions of basic dyestuffs.

Example 11

172 parts by weight of metanil amide are dissolved in 3000 parts of water while adding 45 parts by weight of sodium hydroxide. Into this solution all at once at room temperature a paste made of 413 parts by weight of diphenyl-p,p'-disulfochloride and water by intimate grinding is introduced. The condensation is now carried out exactly as described in example 1, and also the working up of the reaction mixture is done in the same way. It results a reddish powder of the properties of the products obtained in the preceding examples. Constitutively the body is formed by a multiple linking up of the following "structure element":

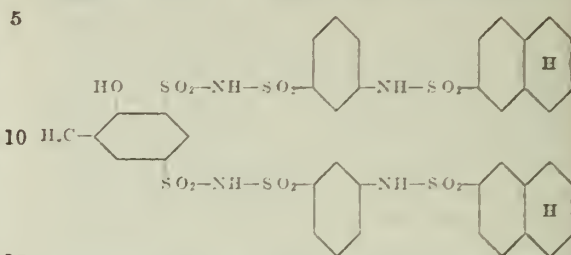


Example 12

133 parts by weight of 4-hydroxy-5-methylbenzene-1,3-disulfamide (obtained from the corresponding disulfo-chloride in a benzolic or ethereal solution by introducing ammonia-gas while cooling) are dissolved in 1500 parts of water while adding 45 parts by weight of sodium hydroxide. Now at room temperature 222 parts by weight of m-nitrobenzene-sulfochloride pasted with water is added, whereupon the condensation is performed as per example 1, by maintaining the reaction mixture constantly alkaline by means of soda lye and gradual increasing of the temperature. As soon as at 90°C a clear solution is got which remains slightly alkaline hydrochloric acid is carefully added till the reaction becomes litmus-acid, whereupon while stirring the solution is poured in a boiling mixture of 200 parts by weight of pig-iron chips, 1000 parts of water and 10 parts by weight of glacial acetic acid. When the reduction is terminated the reaction mixture is made alkaline by means of soda and filtered.

In the filtrate the amount of amino compound is determined by means of a standardized nitrite solution and after cooling for each gramme-equivalent of amino compound 231 gr of a technical mixture of the two isomere tetrahydronaphthalene-sulfochlorides are added which were ground with water to form a paste. The second

condensation is performed exactly as the first and the final product consisting predominantly of a compound of the following constitution-formula:



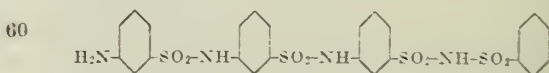
is separated in the usual way from the reaction mixture by acidifying, then filtered and dried. The obtained resin is dissolved in water under an addition of buffer substances such as sodium acetate or sodium bicarbonate, so that a pH-value of about 3 to 4.5 is obtained. This solution has excellent tanning properties.

Example 13

312 parts by weight of m-aminobenzene-benzene-disulfimide are dissolved while warming in 1500 parts of water under addition of 40 parts by weight of sodium hydroxide. To the solution cooled down to 20° a paste is added which is prepared by stirring 244 parts by weight of m-nitrobenzene-sulfochloride with 125 parts of water. The acid being free is neutralized by gradually adding soda lye. Now the mixture is slowly heated to 90-95° and if necessary neutralized with soda lye once more. When it was determined by means of a diazotising test that no remarkable amounts of amino compounds are present 300 parts by weight of sodium chloride are added and the condensation product is precipitated by acidifying with hydrochloric acid at 70°. After cooling the precipitated liquid resin is separated from the acid water and is dissolved in 800 parts of hot water under addition of a sufficient amount of soda lye for neutralizing.

Now for the reduction of the nitro group the hot solution is poured in a boiling mixture of 200 parts by weight of pig-iron chips, 750 parts of water and 7.5 parts by weight of glacialacetic acid, the iron is precipitated by soda and in the filtrate the amount of the amino compounds is determined.

Hereupon the obtained amino compound is condensed with m-nitrobenzene sulfochloride in the above described manner and the nitro compound thus formed is reduced with iron and acetic acid. The solution from which the iron is separated off contains the metanilyl-metanilyl-metanilyl-benzene sulfamide of the following structural formula



in the form of the mono sodium salt. The output related to the metanilyl-benzene sulfamide used amounts to 80% of the theory. The weight of the soda alkaline solution may amount to 2400-2500 parts by weight.

For the condensation with cyanuric chloride to the solution carefully hydrochloric acid is added till the reaction is only in traces litmus alkaline and the solution is cooled with ice. A semiliquid resin is precipitated from which the aqueous solution is poured off. In the solution 53 parts by weight of cyanuric chloride dissolved in 230 parts by volume of acetone are stirred in

at 0-5°. Now the resin is added, whereupon the solution is made weakly litmus alkaline by addition of sodium bicarbonate. The solution is slowly warmed up to 90° while keeping the reaction of the mixture litmus alkaline by gradually adding sodium bicarbonate. Hereupon at 90-95° soda is added until a permanent weakly litmus alkaline reaction is attained. Now the solution is cooled down to 70° and the resin is precipi-

tated with hydrochloric acid. The resin which solidifies in the cold, is pulverized, sharply sucked off and dried at 100°. The thus obtained tanning material contains only a small amount of ash and is considerably soluble in hot water. The solubility is increased by the addition of sodium acetate.

WINFRID HENTRICH.
ERIK SCHIRM.



ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING ETHERS AND ESTERS OF CARBOHYDRATES

Jan Lolkema, Hoogezand, The Netherlands;
vested in the Alien Property Custodian

No Drawing. Application filed February 25, 1941

The invention relates to a method of producing ethers, esters and mixed ether-esters of carbohydrates, more particularly of starch in a dry form which are soluble in cold as well as in hot water.

There are already known several methods of producing alkyl ethers of starch. In general they are obtained by treating an aqueous suspension or paste of the starch with the alkylating agent, e. g. an alkyl sulphate, in the presence of a substance having an alkaline reaction. According to these methods the ethers are generally obtained in the form of colloidal solutions or pastes which can be used as adhesives. The production of the solid ethers in a dry condition from these reaction products is known likewise; for this purpose, however, comparatively laborious and expensive treatments were necessary, such as e. g. precipitation with alcohol, separation by dialysis or separation by adding inorganic salts with subsequent filtering, washing and drying. The products thus obtained were readily soluble in cold water, but only slightly soluble in hot water. Up to the present the said starch ethers have been but little used for technical purposes, which is partly due to the laborious methods of producing the same.

The production of ethers of other carbohydrates and of esters of carbohydrates is also known. Up to the present, however, they have also proved to be of small importance in actual practice.

The present invention relates to a method which renders it possible to produce in a very simple and economical manner from starch and other carbohydrates which may be made into a solution or paste by stirring them with a small proportion of water, ethers, esters and mixed ether-esters in the form of dry flakes or powders which are readily soluble in cold and/or hot water. This method consists in that a mixture of the carbohydrate with a limited quantity of water either after the etherification or esterification or in any desired stage of the said processes, is suddenly heated for a short time to a high temperature and pressed out or spread out to form their layers which are simultaneously dried. If gelatinizable carbohydrates are used as a starting material the reaction mixture is preferably heated to a temperature above the gelatinizing temperature.

The invention is chiefly important for the production of valuable products from starch or starch containing materials and starch derivatives, but it may also serve for the production of ethers and esters from other polysaccharides which likewise will produce viscous, sticky solutions both in cold and hot water.

The invention will now be described with regard to the production of starch ethers.

According to an embodiment of the invention

the starch is first mixed with a small proportion of water (i. e. the proportion usual for the production of cold swelling starch) and with the chemicals required for etherification and, preferably after the etherification process has proceeded to a smaller or larger extent, subjected to the heating process described above.

This process may be carried out by stirring the starch e. g. with from $\frac{1}{2}$ –2 parts by weight of water and subsequently adding the quantity of the alkaline substance required for the reaction. As such e. g. alkali hydrates, salts having an alkaline reaction, ammonia or organic bases may be used. The addition of the said alkaline substances is necessary in most cases for effecting the reaction with the etherifying agent.

The etherifying agent e. g. a dialkyl sulphate is now added, while stirring to the said mixture. In order to accelerate the reaction, the reaction mixture may be heated, but since the reaction is exothermic, this generally will not be necessary and in some cases cooling is even advisable, in order to retard the reaction.

The mixture is now suddenly heated during a short time to a high temperature and pressed or spread out to form thin layers which are simultaneously dried. This operation which is well known from the manufacture processes of cold swelling starch of which it forms an essential part is preferably carried out by applying the mixture to rotating cylinders heated to a temperature of 100° C or above, which are positioned so that the mass is pressed into a thin layer. The starch will thereby be gelatinized in so far gelatinizing has not yet been effected by the alkali during the pre-treatment, and simultaneously dried, so that the material leaving the cylinders will consist of thin sheets or chips which may be ground, if desired.

Before the mass is submitted to this treatment, a more or less advanced etherification of the starch has already taken place; preferably operations are carried out in such a way that the reaction will be accomplished for three quarters or more before the material is heated and dried on the cylinder.

During this latter treatment the etherification process will proceed, particularly because of the fact that owing to the evaporation of the water the concentration of the unreacted part of each component will increase very quickly, whereby the reaction will be considerably accelerated. It has accordingly been found that the etherification process is completed within a short time and that in a few minutes a dry product of the desired degree of etherification is obtained. The method according to the invention therefore renders it possible to utilize the etherifying agent as completely as possible in a very simple and expensive way.

Instead of immediately adding the entire quantity of alkaline substance to the starch-water mixture, it is also possible to add the same entirely or partly together with the etherifying agent. It is also possible first to mix the starch with the water and the etherifying agent and subsequently to add the required quantity of the alkaline substance.

The etherifying agent may be diluted, if desired, with a solvent; this solvent, however, must not have too high a boiling point, as it will have to evaporate again during the treatment on the cylinders.

According to another embodiment of the invention the etherifying agent is made to react with the starch, after the same has been submitted to the above mentioned heating process. This is done preferably by mixing the starch with a small proportion of water and the alkaline substance, subjecting this mixture to the heating treatment in question and subsequently treating the dry product thus obtained with an etherifying agent either or not diluted with an organic solvent. During this treatment the reaction mixture may be heated or cooled if necessary.

This method is particularly suitable for being applied in cases in which the etherifying agent is insoluble in water, or decomposes in the presence of water or for other reasons cannot be added to the aqueous solution of the starch prior to the drying treatment. It is advantageous in that case to dissolve the etherifying agent in an organic solvent and to cause the dry mass obtained by the heating treatment to react with this solution. If desired the solvent remaining in the dry mass after the mechanical removal of the excess solvent may be recovered by evaporation and condensation.

The best known and chiefly used etherifying agents are the esters of the corresponding alcohols e.g. with acids such as sulphuric acid. In the etherifying process this acid will be partly or entirely liberated and for this reason it is generally necessary to add alkaline substances which combine with the acid. It is, however, also possible to employ etherifying agents which do not produce acids, such as the epoxy alkanes. Nevertheless it will be advantageous in this case also to add alkaline substances as they will act as catalysts. After the reaction has been completed, the alkaline substance may be partly or completely neutralized.

The alkyl groups which may be combined with the starch by the etherifying process may be of a varying character and they may contain various substituents, e.g. one or more hydroxyl groups, mercapto groups, rhodanide groups, halogen atoms, amino or substituted amino groups, carboxyl groups or arylcarboxyl groups or alkali salts respectively, alkaline earth salts or other salts or functional derivatives thereof, such as amides and substituted amides, sulphonic acid groups or aryl sulphonic acid groups, or salts or functional derivatives thereof and the like.

The alkyl groups furthermore may have straight or branched chains which may be interrupted by oxygen, nitrogen or sulphur.

The starch may also be etherified with different groups. In that case the starch is reacted with two or more etherifying agents which may be added either simultaneously or successively

and in any desired sequence, either in immediate succession or at given intervals. Examples of such mixed starch ethers are the methyl-ethyl ether and the methyl-hydroxy-2 ethyl ether.

The invention has been described above for the production of starch ethers, but the esters may also be prepared in a similar manner, e.g. by mixing the starch with a small proportion of water and an alkaline substance, subsequently adding an acid chloride and after the reaction has proceeded for a considerable part, heating the mixture on cylinders in the manner described above.

The esters may be derived from polybasic inorganic acids and from mono- or polybasic organic acids, which may belong to aliphatic or the aromatic series. These acids also may contain one or more of the above mentioned substituents.

Furthermore it is also possible to produce mixed ether-esters by treating the starch both with etherifying and esterifying agents. If the addition of the esterifying agent occurs simultaneously with or after the addition of the etherifying agent, the esterifying agent may react with free hydroxyl groups of the starch as well as with certain groups, e.g. hydroxyl or amino groups present in the etherifying agent either before or after esterification, or with both.

Similar derivatives as described above in connection with starch may also be produced from starch products as soluble starch, dextrine and the like, and from other carbohydrates, such as inuline, sugars, different kinds of gums, such as gum arabic, and the like, in so far as they can be made into a solution or paste by stirring the same with a small proportion of water, and the products thus obtained are likewise soluble in cold and/or hot water. By a small proportion of water I mean the proportion generally used in the manufacture of cold swelling starch. Of course mixtures of different carbohydrates may also be used as starting materials.

The methods of production described above are extremely simple, practical and far less laborious than the methods used up to the present, which renders the final products less expensive.

When compared with the usual starch products used for technical purposes e.g. the well known soluble starches, cold swelling starches, dextrines and the like, the starch ethers and esters according to the invention have different properties, which makes that they have special advantages for various purposes. Depending on the nature and/or the quantity of the etherifying or the esterifying agent used per unit of glucose, one obtains products which dissolved in water to a colloidal solution will show a great variety in regard to viscosity. The said viscous colloidal solutions are characterized by a gum-like character and a great and lasting transparency; they do not show retrogradation phenomena and in many cases will possess a better solubility and a strong adhesive power.

They furthermore have the advantage that they are not substantially attacked by micro-organisms, so that practically no preservations need be added to the adhesives produced from the said ethers and esters. Moreover the starch products thus produced will practically form no lumps when dissolved in cold water, a drawback which as is known, is generally inherent to cold swelling starch products.

JAN Lolkema.

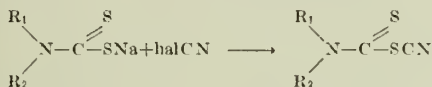
ALIEN PROPERTY CUSTODIAN

PROCESS FOR MANUFACTURE OF SENEVOLS

Jean Claudin, Paris, France; vested in the
Alien Property Custodian

No Drawing. Application filed March 4, 1941

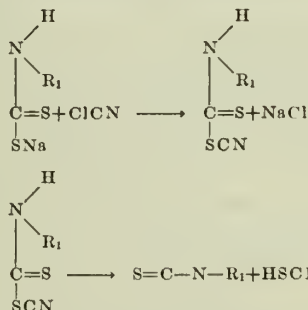
When a halogenide of cyanogen is caused to react upon a dithiocarbamate, a symmetrical monosulphide of thiuram is obtained at the room temperature. It is furthermore known that when the reaction is effected at a sufficiently low temperature, practically in the neighborhood of 0° centigrade, there is observed an intermediate compound according to the following reaction:



in which R₁ and R₂ are any organic radicals. Such compounds may be considered as mixed anhydrides of a dithiocarbamic acid and cyanic or thiocyanic acid. They can be condensed with a second molecule of a dithiocarbamate to lead to monosulphides of thiuram.

I have found that, when a dithiocarbamate derived from a primary amine is used as starting material, the reaction follows another way.

There is readily conjectured the formation of the mixed anhydride by action of a molecule of cyanogen halogenide upon a molecule of dithiocarbamate. But such anhydride is certainly less stable than those responding to the above indicated formula, for it immediately disintegrates by splitting into the corresponding senevol and sulphocyanhydric acid. The reactions proceed according to the following scheme:



It will, therefore, be sufficient to introduce an halogenide of cyanogen into a solution of a dithiocarbamate derived from a primary amine, until disappearance of the totality of the latter, in order to obtain senevols.

In the course of the introduction of halogenide of cyanogen there occurs a turbidness and the senevol sought for progressively separates at the same time as there is observed the presence of

sulphocyanhydric acid in increasing quantity. This reaction of production results in quantitative yields and in products of very good quality.

The following examples are given for the purpose of illustration, but not of limitation, in order to show how the invention may readily be carried into practical effect.

EXAMPLE I.—Production of phenylsenevol

93 grams of aniline are transformed into phenyldithiocarbamate according to any of the known processes by mixing aniline, water, carbon sulphide and the alkaline agent. The solution is filtered, whereafter chloride of cyanogen is introduced. The aqueous liquid becomes turbid, then phenylsenevol is progressively separated, while the formation of sulphocyanide is observed in the aqueous liquid. When all dithiocarbamate has disappeared (drop-tests with perchloride of iron), the further introduction of chloride of cyanogen is stopped and the oil decanted and distilled. After one single distillation there are obtained 120 grams of phenyl-senevol in pretty nearly pure state.

EXAMPLE II.—Production of O-tolylsenevol

By replacing aniline used in the preceding Example with 107 grams of O.toluidine and by operating as per above there are obtained 140 grams of O.tolylsenevol.

EXAMPLE III.—Production of α-naphtylsenevol

By replacing aniline used in the Example I with 143 grams of α-naphtylamine there are obtained 150 grams of α-naphtylsenevol in crystalline state. By one single crystallisation in alcohol there are obtained the fine characteristic needles of P.F.=57° Centigrade.

EXAMPLE IV.—Production of β-naphtylsenevol

When chloride of cyanogen is introduced into a solution of β-naphtyldithiocarbamate there is obtained β-naphtylsenevol in gray flakes which, when recrystallized in alcohol, had the P.F. 61° centigrade.

In all of the previous Examples the introduction of halogenide of cyanogen is stopped whenever it is observed that, by drop-test with ferric chloride, all brown colouring due to dithiocarbamate has disappeared to leave but the characteristic red colouring due to ferric sulphocyanide.

JEAN CLAUDIN.

ALIEN PROPERTY CUSTODIAN

POLYAMIDES

Paul Möller, Dessau, and Hans-Joachim Nicolai,
Dessau-Haideburg, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed March 13, 1941

Our present invention relates to polyamides, and in particular to a new method for preparing hydrophilic superpolyamides.

In our co-pending application Ser. No. — (corresponding with the German application I 66 310 IVd/12o) it has been disclosed that hydrophilic polyamides may be produced by condensing ω -monoaminomonocarboxylic acids having at least four carbon atoms between the amino group and the carboxyl group or the derivatives thereof as, for instance, lactams, esters, or amides in the presence of an inorganic acid. According to the acid content one obtains polymeric substances which are water-swellable or yield a colloidal aqueous solution or are transformed from the sol-state of the warm aqueous solution into the gel-state on cooling.

This invention is based on the observation that under similar conditions the reactants of the superpolyamides, i. e. diamines and dicarboxylic acids having long chains or the derivatives thereof, likewise yield hydrophilic, water-soluble condensation products in the presence of inorganic acids.

While polymers stable on boiling and insoluble in water and in usual solvents are obtained by the condensation of the diamines and dicarboxylic acids having long carbon chains, a content of more than 0.1 mol of inorganic acid anion in the polymer effects that the condensation products are capable of strongly swelling in water, alcohols or other hydrophilic solvents or dissolving therein.

As reactants with a long carbon chain mixtures of diamines or derivatives thereof having at least five carbon atoms between the amino groups and dicarboxylic acids or derivatives thereof (if desired substituted by aliphatic or cyclic radicals) having at least four carbon atoms between the carboxyl groups.

As inorganic acids the halogen hydracids are preferably employed. The process of the invention may also be accomplished with other monobasic mineral acids as, for instance, nitric acid or with polybasic inorganic acids.

The condensation or polymerization is conveniently carried out by heating at 200–250°C in the absence of air. It is not necessary to use a special catalyst since the mineral acid already effects a sufficient acceleration of the condensation procedure. The acid is preferably added in the form of the salt of the diamine to be condensed or a derivative thereof.

It is also possible to prepare interpolyamides in which case the choice of the reactants depends on the intended use and may be made regardless of the desired sensitivity to water since

this factor is solely controlled by the mineral acid used.

The new polyamides are used in various forms and for many purposes as, for instance, for gelatin substitutes binding agents, sizing and finishing agents, and thickening agents for printing pastes.

The more detailed practice of the invention is illustrated by the following examples. There, are, of course, many forms of the invention other than these specific embodiments:

Example I

80 g of hexamethylenediamine adipate and 20 cc of concentrated hydrochloric acid (37.8%) are intimately mixed and heated together in an atmosphere of carbon dioxide at 211–222°C during 20 hours after the air is carefully removed by carbon dioxide. The product thus obtained is yellowish brown and soluble in water and methanol.

If the amount of hydrochloric acid is decreased, water-insoluble polymers are obtained.

Example II

75 g of hexamethylenediamine adipate and 23 g of ϵ -aminocaproic-acid-hydrochloride are intimately mixed and condensed in the same way as described in Example I. The thus resulting product is yellowish brown and soluble in water and hot alcohols.

If the amount of ϵ -aminocaproic-acid-hydrochloride is decreased, products are formed which have a small solubility in water.

Example III

60 g of hexamethylenediamine adipate, 40 g of ϵ -caprolactam and 50 g of ϵ -aminocaproic-acid-hydrochloride are polymerized in the manner as described in Example I. The polymer thus prepared is a tenacious transparent yellow product soluble in water and aqueous alcohols.

If the amount of ϵ -aminocaproic-acid-hydrochloride is lowered to 6.5g, a milky water-insoluble polymer is produced.

Example IV

A mixture of 60.6 g of sebacic acid, 25.9 g of hexamethylenediamine and 23.4 g of hexamethylenediamine hydrobromide is melted and heated at 225°C for 15 hours in absence of air. The polymerization product is a slightly yellow and very tenacious mass soluble in water and warm methanol and can be worked up into transparent films.

PAUL MÖLLER.
HANS-JOACHIM NICOLAI.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR SEPARATING UNSAPONIFI- ABLE COMPOUNDS FROM OXIDATION PRODUCTS OF HIGHER MOLECULAR HY- DROCARBONS

Karl Blass, Magdeburg, and Otto Bruecke, Hoch-
speyer/Pfalz, Germany; vested in the Alien
Property Custodian

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This invention relates to a process for separat-
ing unsaponifiable compounds from oxidation
products of higher molecular hydrocarbons.

The oxidation of higher molecular hydrocar-
bons, such as paraffingatsch, is directed in such
a manner that the products, besides fatty acids
and similar compounds, contain considerable
quantities of unsaponifiable hydrocarbons which
may amount to 60% and more. It is known to
separate unsaponifiable compounds from the oxi-
dation products by distilling after saponification
of the fatty acids, etc. the volatile constituents
from the soaps. Before or after separation of
the unsaponifiable compounds, which may be
effected of course by other methods than distilla-
tion, the fatty acids have also been saponified
and then heated up to approximately 280-350° C. so
as to convert oxyacids, lactones lactides, estolides
and other polymeric esters formed in oxidation
into fatty acids. In this known procedure heat-
ing required approximately 1 to 10 hours, depend-
ing on the treating temperature.

It is further known to remove volatile con-
stituents from aqueous saponification products of
synthetic or natural fatty acids by heating the
saponification products under pressure beyond
the melting point of the anhydrous soaps. At the
same or a still higher temperature, possibly while
reducing pressure in vacuo or supplying water
vapor or inert gases, the water and the unsaponi-
fiable portions or the other volatile constituents
are driven out by distillation.

The known processes combining with the re-
moval by distillation of the unsaponifiable and
other volatile substances an improvement of the
saponified fatty acids apply high pressures and
require therefore expensive apparatus of rela-
tively low output.

It is an object of invention to eliminate these
disadvantages for this purpose: The oxidation
products of higher molecular, particular aliphatic,
hydrocarbons, as paraffingatsch, etc., are first
saponified, whereupon the mixture of fatty acid
soaps and unsaponifiable substances is freed from
water and then heated up to about 310-350° C.
The absolute pressure at which this treatment is
performed is so adjusted that only a portion of
the unsaponifiable substances is removed by dis-
tillation, and the heating is continued as long as
required for converting the oxyacids, lactones etc.
Then the remainder of the unsaponifiable sub-
stances is distilled off whereby the temperature
may be lowered and the pressure reduced to
vacuum, preferably high vacuum. The treat-
ment according to the invention is preferably

combined with intensive motion, for instance by
rotating the liquid or melt in the vessels and/or
passing steam therethrough.

It has been found that the soap melt as long
as it contains the unsaponifiable substances or
a portion thereof remains in a thinly liquid state
and withstands temperatures up to about 350° C
and over without injury, so that the process ac-
cording to the invention yields, a carefully pre-
served fatty acid of high grade. Owing to the
possibility afforded by the invention of removing
by distillation a part of the unsaponifiable sub-
stances already during the step of heating to
high temperatures, these steps of the treatment
as well as the following ones may be carried out
at greater efficiency. Furthermore, the treating
period is shortened, since while heating to high
temperatures is going on a portion of the un-
saponifiable substances can be distilled off and
the removal by distillation of the remaining por-
tion may be effected immediately after heating.
Finally, as part of the considerable amount of
heat still retained by the highly heated melt is
utilized for distilling off the unsaponifiable sub-
stances, the heat economy is generally improved.

If on the other hand according to known meth-
ods the dry molten soap is highly heated in the
absence of diluents and kept for the necessary
time at the high temperatures required for im-
proving fatty acids, uneven heating as well as
local overheating of the soaps is unavoidable with
the result that the soaps are injured by partial
decomposition. The yield of fatty acids and the
color thereof are particularly affected.

When in the process according to the inven-
tion, after the refinement of the fatty acids, the
unsaponifiable substances are distilled off in a
high vacuum, the temperature of distillation may
be correspondingly reduced, whereby the soap
melt from which the unsaponifiable substances
are more and more withdrawn during distillation
and which thus becomes more sensitive to high
temperatures is preserved still more. After the
unsaponifiable substances have been removed by
distillation the temperature of the soap melt is
reduced in known manner, for instance by passing
therethrough low pressure steam or injecting
water, but the temperature must still be high
enough to permit removal of the soap in thinly
liquid condition from the apparatus. It is fur-
ther possible to place the soap after completion
of distillation in a vacuumized autoclave equipped
with agitators and heating means and then to
eliminate the vacuum by steam developed for in-
stance from introduced water. By the further

supply of water to the autoclave, for instance under pressure, the melt can be converted into an aqueous soap, the temperature of which may be correspondingly reduced, the pressure in the autoclave being easily regulatable by blowing off steam. The liquid soap can then be conveyed to a plant in which the soaps are decomposed, for instance by adding mineral acid, and the liberated fatty acid after having been washed with water, etc. in the usual way is worked in a high vacuum distillation apparatus. The distillates obtained are of high grade and have a light color.

Example 1

Paraffingatsch obtained by the Fischer-Tropsch-synthesis from carbonmonoxide and hydrogen is oxidised in known manner to crude fatty acids which contained considerable portions of unoxidised or partly oxidised products. To the products of the oxidation the quantity for sodium carbonate solution of 30° Bé. theoretically required for the saponification of the fatty acids contained in the products is added in an autoclave provided with agitator and heating means. After the sodium carbonate solution has acted upon the fatty acids, soda lye of 40° Bé. to the extent of 10% of the amount of alkali theoretically required for saponification is added and while the contents of the autoclave are heated saponification is completed at a pressure of 7 atmospheres. The mixture of fatty acid soaps and unsaponifiable substances kept liquid by corresponding heating is then dehydrated under pressure, whereupon the molten mixture is placed in a distilling vessel equipped with heating means, agitators and steam spray and heated therein in vacuo up to about 335° C while it is thoroughly stirred and water vapor passed through it. This temperature is maintained for two hours and the vacuum so adjusted that during heating and the conversion of the oxyacids, lactones etc. to fatty acids approximately one-half of the unsaponifiable substances is distilled off, chiefly the lower boiling portions of the distillable substances present passing over.

The mixture treated as described had been obtained by the oxidation of crude paraffin boiling between 320° and 450° C. The content of acid oxidation products of the mixture amounts to approximately 40%.

While the mixture is heated up to about 335° C the presence of the unsaponifiable substances has the effect of keeping it in thinly liquid condition, so that uniform heating is insured and local overheating or decomposition of the molten mixture cannot occur. After the fatty acids have been refined by heating the steam is shut off and a high vacuum gradually produced in the distilling vessel, so that everything distillable still present in the mixture is driven off. Owing to distillation the temperature of the contents of the vessel is lowered. When it has reached about 290° C, heating is started again and distillation completed at this temperature. The soap melt is then placed in a vacuumized vessel provided with agitator and heating means and constructed as autoclave. Into the soap melt water is introduced, f. i. by a pump, until the water vapor

produced has destroyed the vacuum and a pressure regulatable at will by blowing off vapor develops in the autoclave. The soap melt absorbs water and gradually changes into an aqueous liquid soap while its temperature is considerably reduced. From the autoclave the soap solution is passed to another plant in which it is decomposed by sulfuric acid, whereupon the fatty acid so produced can be distilled in known manner.

Example 2

Starting material of the kind referred to in Example 1 is mixed in a similar saponifying apparatus with the requisite amount of 40° soda lye and simultaneously heated. The steam pressure developing in the autoclave is kept at 5 atmospheres. After the saponification of the fatty acids the mixture of soap and unsaponifiable constituents is sucked into a vacuumized distilling apparatus provided with heating means, stirring device and steam spray, the stirrer being in operation during suction. While the mixture is being drawn in, the main part of the water contained in the soap is evaporated. When the heating coil is covered with the mixture of soap and unsaponifiable constituents, the heating is turned on and superheated steam passed through the spray. A short time after having been sucked in, which requires about 15 minutes, the mixture is free from water and by continual stirring and the passage of water vapor is brought to a temperature of 325° C. The vacuum is so adjusted that during heating and the consequent conversion of the oxyacids, lactones, etc. into fatty acids only one-third of the unsaponifiable constituents is distilled off which comprise the lower boiling substances. The contents of the distilling apparatus are kept at a temperature of 325° C. for 3 hours, and the presence of the unsaponifiable constituents has here the same good effect as in Example 1. After refining the unsaponifiable constituents still present are distilled off as described in Example 1, and the soap melt is drained into a vacuumized outfit provided with stirrer, heating means and steam spray, whereupon it is stirred and low pressure steam passed through it to eliminate the vacuum, and at a steam pressure of half an atmosphere the temperature of the soap melt is reduced to 250–260° C. The soap is then drawn off over a cooling roller or placed in an apparatus wherein it is continuously decomposed into fatty acid and Glauber's salt solution with the aid of sulfuric acid.

Example 3

The procedure was the same as described in Examples 1 and 2, though instead of the sodium compounds mentioned the corresponding potassium compounds were used for saponification, so that after refining and distilling off the unsaponifiable constituents the soap melt could be cooled down to 150° C. and was found to be still liquid.

Similar advantages are obtainable if saponification is performed with mixtures of sodium and potassium compounds.

KARL BLASS.
OTTO BRUECKE.

ALIEN PROPERTY CUSTODIAN

SUBMARINE PAINT

Erich Baumheier, Oschatz-Zschollau, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed March 8, 1941

This invention relates to an improved submarine or underwater painting for the hull of vessels, for bridges, and for any other submarine constructions or underwater structures consisting, e. g., of brickwork, wood, concrete or iron.

It is an important object of the present invention to provide a paint by which aquatic or marine animals or plants are efficiently prevented from growing to the underwater surfaces.

A special object of the invention is to provide a paint which is not reduced in efficiency by the fact that marine animals, such as, shells and lepadides may get accustomed to the antidote or poison contained in the paint.

Another object of the invention is to provide a paint of a very uniform composition.

With these and further objects in view which will be apparent from the following disclosure, my paints contain an admixture of the poisonous substance contained in croton oil which is sometimes referred to also as physic-nut oil. I have found that paints containing said poisonous substance are extremely efficient with a view to preventing adhesion of organic matter to the painted underwater structure.

Any paints which are suitable as an anti-fouling or underwater painting may be used in connection with the invention. In order to incorporate the poisonous matter in the paint, the croton oil proper may be admixed thereto. However, since this oil contains only comparatively small proportions of active poisonous substance, I prefer adding the poisonous matter after its separation from the croton oil.

According to a further feature of the invention, a powder material such as carbon, especially in the form of charcoal, kieselguhr, alumina or the like, whose particles offer large active surfaces may be charged with the poisonous constituent of the croton oil and admixed to the paint. Such powder admixtures do not produce any substantial difference as to the effect of the poisonous matter, however, the production of the poisonous matter which does not form part of the present invention, is substantially facilitated. The poisonous matter which is sensitive to heat, is originally obtained in the form of a solution in methanol or the like and has to be extracted from the solution by vacuum evaporation. Said vacuum evaporation can be avoided, however, by extracting the poisonous matter from the solution by shaking with substances having large active surfaces, such as carbon or charcoal, kieselguhr and alumina.

It is also possible to embody in the paint a

larger percentage of said poisonous matter by at least partly substituting croton oil for the normal binder of the underwater paint. Moreover, the paints in addition to croton oil or its poisonous matter may contain any of the customary anti-adhesion substances, such as copper or mercury compounds, organic or inorganic arsenic compounds, organic acids or the salts thereof, phenols or phenol derivatives.

I have found that the poisonous matter of croton oil as to its adhesion preventing effect in submarine paints excels the conventional substances which were so far admixed for this purpose. Compared to copper or mercury compounds the poisonous matter of the croton oil offers the advantage that it can be distributed more readily and more uniformly in submarine paints.

The excellent properties of the poisonous matter of the croton oil are probably due to the fact that this poisonous matter on the one hand is only slightly soluble in water, so that it remains active for a long time, while on the other hand it can be dissolved completely and evenly distributed, e. g., in varnish, so that fresh poisonous matter is laid bare on the surface as the paint is gradually rubbed off.

A special advantage of the invention resides in the fact that any adaptation of the organisms producing the deposits, such as is possible with the conventional antidotes, is precluded with the poisonous matter of croton oil.

The poisonous matter may be extracted from the croton oil by shaking the croton oil with methanol, as described in E. Baumheier, Inaug.-Dissertation Leipzig, 1932. To this end, 100 kgs of croton oil may be intensively stirred for ten hours with 100 liters of absolute methanol in a closed stirring device, at room temperature. The liquid is then let stand until the methanol has been clearly separated from the oil, and the oil is removed by a siphon. The methanol solution is then evaporated at 50° C, under vacuum and carbon dioxide current. The methanol may be used over and over again. The poisonous matter of the oil is left behind by evaporating the methanol. The evaporating process may be avoided by extracting the poisonous from the solution by means of substances having large active surfaces, such as, carbon, especially in the form of charcoal, kieselguhr, alumina.

Example 1.—The submarine or anti-fouling paint consists of 60 parts of coumarone resin, 90 parts of tetrahydronaphtalene, 36 parts of a chlorinated caoutchouc-benzol solution (33 per

cent caoutchouc, 67 percent benzol), 20 parts of croton oil, 75 parts of Turkey red or purple oxide of iron and 25 parts of active carbon or charcoal charged with ammonia (all by weight).

Example 2.—The underwater paint is prepared by admixing 180 parts tetrahydronaphtalene, 120 parts coumarone resin, 72 parts of a solution of chlorinated caoutchouc in benzol in a proportion of 1:2, 150 parts of Turkey red and 60 parts of active carbon or charcoal charged with about 3 percent of the poisonous matter of croton oil (all by weight).

Example 3.—The paint is made from 100 parts of croton oil, 40 parts of chlorinated caoutchouc dissolved in benzol in a proportion of 1:2, 100 parts of purple oxide of iron, 1 part lead man-

ganese naphtenate, 0,5 parts cobalt naphtenate and a proportion of tetrahydronaphtalene sufficient to make the paint ready for use.

The method of the present invention has been described in detail with reference to specific embodiments. It is to be understood, however, that the invention is not limited by such specific reference but is broader in scope and capable of other embodiments than those specifically described.

Where the binder is partly replaced by croton oil, the croton oil or its poisonous constituent should be added in a proportion sufficient to substitute the amount of binder which is lacking for producing satisfactory binding action.

ERICH BAUMHEIER.

ALIEN PROPERTY CUSTODIAN

COOLING AND HEATING LIQUIDS

Ludwig Beer, Herbert Berg, and Wolfgang Gruber, Burghausen, Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 10, 1941

The art presents plenty of examples in which the applying of cooling or heating liquids, resp. of liquids causing alternatively cooling or heating would be naturally desired. As for regulations of the temperature which are to act much above 100° the real applying of cooling or heating liquids is relatively seldom; the reason for this lies in the fact that a heating and cooling liquid, favorably to be applied in general, ought to have a great selection of properties, which none of the liquids hitherto taken into consideration possesses: Such a liquid ought to be cheap and unchangeable in continuous operations, it ought to have a high boiling point in order to avoid pressure apparatus, in spite of this, however, it ought to be stable in such a degree that—even at temperatures above 200°—it does not separate incrustations on the cooling or heating surfaces nor should it corrode the surfaces. A great difficulty is added by the fact that usually metallic especially iron surfaces are applied which have a catalytic decomposing effect on most of the high boiling organic substances. Further, in spite of its high boiling point, such a liquid ought to be fluid, possibly thin fluid at usual temperatures. If the cooling or heating requires that the liquid is pumped in circulation, a new requirement is added: the liquid must not destroy lutings, stuffing boxes and the like by unailing resp. by degreasing them.

None of the high boiling liquids hitherto taken into consideration complies with these conditions: e. g. diphenyl proposed for the heating of baking ovens is too much expensive as to be generally applied, beside this it freezes at 70.5°. High boiling oils of the type of tricresylphosphate, of the phthalic acid esters and the like are also too expensive and decompose themselves surprisingly quickly in iron vessels already at temperatures between 150–200°, whereby the heat transferring surfaces become incrustated. Glycerol decomposes itself still more rapidly. Also oils of the type of the superheated steam cylinder oils—alluring naturally by their cheapness—resinify too rapidly. Moreover their large viscosity at usual temperature is a great disadvantage.

Now it has been found that isophoron, which may be obtained very cheaply from the residues of distillation of the manufacture of acetone, comprises in itself all properties desirable for a cooling or heating liquid as described above, exceptional its capacity of dissolving oils which is also common to diphenyl, phthalic acid esters, glycerol and the like. For a great number of applications it represents an ideal heating and cooling liquid.

It is here the question of a completely new suitability opposite to all expectations, because isophoron was expected to incline to decomposition under the conditions taken here into con-

sideration and because this substance resinifies rapidly indeed if being heated in the air. The required exclusion of air, however, may be easily realized in practice.

5 Still more surprising is the further finding that isophoron prevents the decomposition of liquids inclining naturally to decompose at high temperatures if it is added to them. Therefore it is possible at first to apply easily the still cheaper high boiling fraction of the last runnings of the distillation of acetone, e. g. acetone oil boiling between 161 and 187° or between 188 and 211° instead of isolated isophoron. Moreover the possibility is given to add oils properly useless but 10 capable to raise the boiling point, especially those as e. g. the cheap superheated steam cylinder oils which have a lubricating effect on packings and stuffing boxes. By these lubricating oils, made useful by the combination with isophoron according to the invention, it has been possible for the first time—in spite of the natural capability of the isophoron to dissolve oils—to move high boiling cooling and heating liquids in circulation for continuous operations with the aid of pumps. 15 Thus there has been found a method for solving of the difficulties in those cases, when large quantities of heat must be led off or added through relatively small wall surfaces.

Various proposals for apparatus in which heating and cooling liquids may be used have already 20 been made. E. g. a heat exchanger may be mentioned for carrying out exothermal catalytic gas reactions, provided with numerous thin walled tubes vertically arranged for receiving the granulous or powdery contact substance, and with two tube bottoms tightening the ends of the tubes, whereby a middle room provided with two openings—one for leading off and one for adding a refrigerant—is separated from two receivers provided with two openings, one for leading off and one for adding reaction gases. But all these proposals were practically useless if the heat exchange had to be carried out at temperatures above 100°. Only by finding liquids containing 25 isophoron the method of heat exchange can be really applied also in these cases. Hereby superheated zones in the catalyst—causing secondary reactions and soon deteriorating of the catalyst—are avoided. Therefore it is no longer necessary to keep the temperature below the optimum in those parts of the reaction room, entered first by the reaction components, a method known for reducing the capacity of the whole reaction room. By equally regulating the temperature also the great passing through of the reaction components—formerly necessary for avoiding local superheating and thereby reducing the concentration of the reaction products—can be much diminished. By avoiding both disadvantages it is possible to make accessory apparatus much more 30 35 40 45 50 55 60

compendious, e. g. evaporators, preheaters, condensers for reaction products, circulation pumps. At the same time the required expense of heat is importantly reduced.

The way of applying cooling or heating liquids containing isophoron, resp. the equipment of the apparatus to be applied for the heat exchange, depends naturally on the thermal and chemical conditions in each case. E. g. if producing thermally vinyl acetate in the above described tube oven, it has been proved to be useful that the diameter of tubes for the catalysts may not be wider than 50 mm. It has been found that the catalysts can be brought in very comfortably even if the tubes are narrower than 50 mm and that the filling is much more uniform than it would be in wide one tube ovens. The discharging of the used up catalyst from the narrow tubes can also be easily carried out e. g. with the aid of hot water or vapors whereby even no dust is formed. One of the numerous possibilities of applying the new liquids may be illustrated by the following description of producing vinyl acetate:

Example

The well known catalyst, consisting of active carbon, impregnated with zinc acetate was filled into the tubes of a tube oven according to the above mentioned heat exchanger, which was provided with 51 tubes of 35 mm diameter in the clear, of a length of 155 cm and of a capacity of 76 liters; the oil container, provided with inlet and outlet tubes for the cooling and heating liquid, contained about 90 liters. The oil circulated through the apparatus, whereby a pump, a heater and a condenser were used. After removing the air by nitrogen the whole oil system was filled up with a mixture of one part of acetone oil of the boiling point of 183–211° and two parts of superheated steam cylinder oil. In order to condensate the acetone oil which evaporizes at the higher end temperatures, a condenser filled up with nitrogen, was connected with the oil container. Slight boiling did not occur before 210°.

At the beginning of the oil circulation the oil was heated at first up to 160°. Then a mixture of acetylene and vapors of acetic acid, heated in a preheater up to 155°, was blown through the catalyst tubes in such a way, that the mixture entered the apparatus at the bottom and left it at the top. The leaving mixture of gas vapors was freed from the produced vinyl acetate and the abundant acetic acid by a condenser. The acetylene not used up was led back into the process by circulation together with some fresh acetylene after having removed some waste gas. With an acetylene circulation of 7 cbm pro hour and a passing through of 8.2 kg of acetic acid pro hour (relation of acetylene to acetic acid = 100:50, time of stay in the oven 25 sec.) the condensed raw reaction product contained 50% of vinyl acetate. With an acetylene circulation of 7 cbm pro hour and a passing through of only 5.7 kg of acetic acid pro hour (relation 100:35, time of stay in the oven 28.8 sec.) a raw product containing 80–90% of vinyl acetate was obtained. With an acetylene circulation of 8.1 cbm pro hour and a passing through of 5.7 kg of acetic acid pro hour (relation 100:30, time of stay 25.8 sec.) the obtained vinyl acetate concentration was 96%. After 1310 hours the catalyst was not used up. During this time the temperature of

the cooling liquid was gradually increased up to 212°. Correspondingly a complete equally proceeding increase of the temperature up to 213–215° occurred in the reaction tubes. The average production was 1.6 kg of vinyl acetate pro liter of catalyst room and pro day. If working in order to get specially high capacities—which can be attained by giving up an extremely high concentration of vinyl acetate and also by a somewhat quicker increase of the reaction temperature—productions until 2 kg of vinyl acetate pro day and liter can be obtained.

The effect of the regulation of the temperature according to the invention is shown by an extremely equal regulation of the particularly desired temperature in the whole catalyst room. The result is—beside the increase of the output and the concentration—a complete decline of by-products like acetone and ethylenediacetate which otherwise are obtained, and a large decrease of decomposition gases. The obtained vinyl acetate is very much inclined for polymerizing and is especially pure. For instance in the block-polymerization the undesired red color of the polymers does not occur. Eliminating the by-reactions, the life time of the catalyst is naturally prolonged. The packings and stuffing boxes are permanently automatically relubricated. In this process the oven for the reaction and all accessories are much more compendious than those in the method of working hitherto applied.

For comparison: a one tube oven yielded, under the same working conditions but without the described regulation of temperature by oil, only an output of 0.9–1 kg of vinyl acetate pro day and liter catalyst room—the concentrations of vinyl acetate lying between 12–18%—though the passing through was fourfold larger and the relation of acetylene and acetic acid was 100:20. Thereby the obtained vinyl acetate contained already remarkable amounts of acetone and other impurities. Working in this way it is of course also possible to increase the concentration of the produced vinyl acetate by diminishing the passing through and increasing the reaction temperatures, but thereby the output is reduced and the impurities increase importantly.

The application of the new cooling and heating liquids, described above in a special example, can be made suitable in a wide extent for the conditions of other cases and thereby it can be usefully applied for the most different kinds of heating and cooling. E. g. in contrast to the above described method of producing vinyl acetate the cooling liquid may be formed in such a way, that the reaction heat is led off partly or for the most part as evaporation heat into a condenser by using an isophorone, mixed with much lower boiling constituents as cooling liquid. E. g. an acetone oil of the boiling point of 161–187° still contains sufficient isophorone to grant the required stability of the whole liquid mixture.

By usefully applying liquids containing isophorone also the following thermal processes can be improved: e. g. the production of vinyl chloride, of vinyl acetylene, of acrylic acid nitril and the like, condensation reactions as for instance the well known condensation of diamines with dicarbonic acids, polymerizations carried out continuously in tube shaped systems, and the like.

LUDWIG BEER.

HERBERT BERG.

WOLFGANG GRUBER.

ALIEN PROPERTY CUSTODIAN

SOFTENING AGENTS FOR HIGH POLYMERIC SUBSTANCES

Wolfgang Gruber and Hans Machemer, Burg-hausen, Germany; vested in the Alien Property Custodian

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The esters of the fatty acids as cottonseed oil, linseed oil, olive oil, sesame oil or tall oil, of fish oil, coconut oil and the like, practically do not solve highest polymeric vinyl chlorides or nitro-cellulose in the heat and have only slight plasti-fying properties. If trying to produce artificial material of equal parts of polymeric vinyl chlo-ride and oleic acid methyl ester, linseed oil acid ethyl ester or tall oil fatty acid methyl ester at 200-250°, fatty not homogeneous products are formed in which the softener is unbounded. With the double quantity of polymeric vinyl chloride very hard, brittle, and sintered substances are obtained, breaking at 0° and sweating out the softener at room temperature. Therefore a technic working up of these non-solvents with the men-tioned polymeric substances is difficult.

Now it has been found that excellent softeners for highest polymeric substances as polyvinyl chlorides, polyvinyl acetates, cellulose acetates, nitro celluloses, cellulose ethers and the like, may be obtained if the double bounds in the esters of the above mentioned fatty acids are removed wholly or partly and—according to the known method of work—hydroxyl groups or hydroxyl and chlorine or, if necessary, also only chlorine is added and the groups led in are substituted, e.g. acylated and/or alkylated.

Such derivatives of the mentioned unsaturated fatty acids can be produced as follows:

Example 1

10 parts of oleic acid are oxidized with 3 parts of potassium hydroxide in 25 parts of water and 10 parts of potassium permanganate in 25 parts of water in the course of 24 hours at 0-10°. From the filtrate a solid acid is separated by acid-ifying which proves to be trans-9.10-dihydroxy stearic acid (melting-point 134°) after recrystal-lizing with alcohol. By esterifying this acid with methyl alcohol containing hydrogen chloride, trans-dihydroxy stearic acid methyl ester, (melt-ing point 106°) and by boiling it with acetic acid anhydride in excess and sodium acetate as a catalyst trans-9.10-diacetoxy stearic acid methyl ester (boiling point at 0.8 mm: 201°) are ob-tained.

Example 2

10 parts of oleic acid are oxidized in 40 parts of glacial acetic acid with 4 parts of 30%ic hy-drogen superoxide for one hour under reflux, and after adding 10 parts of glacial acetic acid and 2 parts of 30%ic hydrogen superoxide it is oxidized further for one hour under boiling. The residue of evaporation yields after saponifying

and acidifying cis-9.10-dihydroxy stearic acid (melting-point: 95-98°), which is esterified with methyl alcohol containing hydrogen chloride to cis-dihydroxy stearic acid methyl ester (melt-ing point: 72-74°) and is acetylated with acetic anhydride in excess and sodium acetate to cis-diacetoxy stearic acid methyl ester (boiling-point at 2 mm: 221°).

The corresponding butyl ester can be produced as the above mentioned methyl ester with the ex-ception that the esterification is carried out with butyl alcohol containing hydrogen chloride. In the same way ethoxy buthyl ester may be pro-duced by esterifying with ethoxy butyl alcohol containing hydrogen chloride.

Example 3

100 parts of tall oil (boiling point at 3 mm: 185-230°) with the acid number of 162 and the iodine number of 180 according to Smit, 189 ac-cording to Hanus, are solved in 60 parts of potash lye in 5000 parts of water and oxidized under stirring with 200 parts of potassium permanga-nate/5000 parts of water at about 5° in the course of 24 hours. From the filtrate the acids soluble in water are separated by acidifying, and by recrystallization with alcohol a crystallized acid (melting point: 132°) with the acid number of 179 is obtained. The esterification with ethyl alcohol containing hydrogen chloride and the following acetylation with acetic anhydride and sodium acetate yield the acetyl derivative of a hydroxylized fatty acid ethyl ester (boiling point at 0.7 mm: 215°).

Example 4

100 parts of tall oil according to Example 3 are boiled in 800 parts of glacial acetic acid with 80 parts of 30%ic hydrogen superoxide for one hour in reflux and further oxidized after an ad-dition of 200 parts of glacial acetic acid and 40 parts of 30%ic hydrogen superoxide for one hour. The residue of evaporation yields after saponi-fying with soda lye and acidifying a hydroxylized fatty acid unsoluble in water with the iodine number of 43. It is esterified with methyl al-cohol containing hydrogen chloride, and the resi-due of evaporation is acetylated with acetic anhydride in excess and sodium acetate for 2 hours under reflux. After separating the mean of acidylation and washing and drying an ester free from hydroxyl groups is obtained with the acid number of 16, esterification number of 230 and iodine number of 60.

Example 5

10 parts of oleic acid are solved under stirring in 5 parts of sodium carbonate/50 parts of water and treated at 0° with 2.7 parts of chlorine. The hydroxy chlorine stearic acid, precipitated after acidifying, yields by esterification with methyl alcohol containing hydrogen chloride and after neutralizing a residue of evaporation with 12.6% of chlorine after being dried in vacuum. After boiling for four hours with acetic anhydride in excess and sodium acetate as a catalyst an acetylated acid ester of 11.3% of chlorine free from hydroxyl groups is obtained. Producing these esters, oleic acid methyl ester, being afterwards oxidized and acetylated as above described, may be used as starting material.

Example 6

10 parts of tall oil fatty acid methyl ester (boiling point at 1 mm: 180–185°) are stirred at 0° with the solution of 6.4 parts of sodium carbonate in 60 parts of water and treated with 4.5 parts of chlorine. The reaction product is washed and dried. An ester containing 20.3% of chlorine is obtained changing into an ester of 18.5% of chlorine by being treated for 2–3 hours with acetic anhydride in excess and sodium acetate.

Example 7

10 parts of oleic acid methyl ester (boiling point at 2 mm: 185–200°) are chlorinated in 10 parts of petrol ether under stirring and cooling until chlorine can be identified in the waste gas. After neutralizing by washing in ice water and drying in vacuum at 150° a chlorinated derivative of the ester of 38.1% of chlorine is obtained.

If 6 parts of the chlorinated ester are boiled for some hours in 10 parts of methyl alcohol at 100° with 0.8 parts of sodium in 25 parts of methanol, hereafter washed and dried in vacuum, a substance of 8.6% of methoxyl and 22.8% of chlorine is formed.

Example 8

10 parts of tall oil fatty acid methyl ester (boiling point at 1 mm: 180–185°) are chlorinated in 10 parts of petrol ether under stirring and cooling until the saturation of the C=C bonds. After neutralization by washing and drying an ester of 31.8% of chlorine is obtained.

The derivatives of unsaturated fatty acids of high molecular weight, produced according to the above described examples, are excellent softeners for high polymeric substances, especially for highest molecular polyvinyl chloride. The capacity of these esters for solving polyvinyl chloride is—in contrast to the not substituted saturated fatty acid esters—so strong that generally it is not necessary to add other softeners like trikresyl phosphate or phthalic acid esters. The mentioned esters give the polyvinyl chloride above all excellent cold stabilities. In this sense the esters of the diacetoxy stearic acids, according to the examples 1 and 2, are especially suitable, above all the butyl and especially the ethoxy butyl esters according to example 2. The ester mentioned at last are also suitable to improve the somewhat imperfect cold stability of the only chlorinated esters which easily can be got according to examples 7 and 8, so that they are satisfying in all respects. Not only the esters themselves and their mixtures are excellent softeners for polyvinyl chloride, but it has been proved that extraordinary good effects, specially according to the cold stability, can be obtained with

mixture containing intermediate products as components of mixture, which are obtained by producing the esters as described in the examples. Thus an artificial substance of 3 parts of polyvinyl chloride, 2 parts of diacetoxy stearic acid methyl ester and 1 part of tall oil fatty acid methyl ester has a cold stability of –60°. This material is not greasy and is extremely elastic. An addition of dihydroxy stearic acid to the esters described in the examples improves the smoothness of artificial material of polyvinyl chloride and facilitates spattering. Even considerable amounts of unsaturated resp. saturated fatty acid esters may be employed with. An addition of chloronaphthalene improves the heat stability of these materials.

The pressed masses produced at 180–200° can be also easily welded, because in consequence of the high boiling point and the favorable properties of solving no carbonization of the softener occurs and the welded spots are often scarcely to be distinguished when the material is cut. In consequence of the great cold stability the products are especially suitable for those manufactures requiring elasticity and bending strength in the cold. The resistance to pressure, resistance to tearing, resistance to notch, and the resistance to abrasion is considerable. The halogen adheres much better to the chlorinated products than to the low molecular fatty acids.

In the examples oleic acid and tall oil fatty acids were always used as starting materials. All oils mentioned in the introduction, however, may also be applied as starting materials. Thus e. g. the linseed oil acid may be oxidized by potassium permanganate in diluted alkaline solution to a tetrahydroxy fatty acid, the sativine acid, and this may be esterified and acetylated and/or alkylated. These derivatives are also excellent softeners for high polymeric substances.

As cold stability the temperature is named at which the pressed mass can still be bended. About 10° lower the product becomes brittle and breakable.

The application of the above described softeners in particular may be demonstrated by the following examples:

Example 9

100 parts of polymeric vinyl chloride are kneaded with 100 parts of trans-diacetoxy stearic acid methyl ester and then the mixture is worked up in the known way under employing pressure and heat to plates, rods, tubes, hoses, threads and commodities which are very smooth and elastic and have the resistance to cold of –39° and the resistance to heat of 150 minutes/170°. The softener does not sweat out in the heat. The masses can be easily welded in the heat. An addition of dihydroxy stearic acid (10%) improves the resistance to cold up to –43°, improves the smoothness and facilitates the spattering.

Example 10

Waste leather, asbestos, cellulose, paper, pasteboard, cork, and the like are kneaded with a solution consisting of 10% of polymeric vinyl chloride and 8% of diacetoxy stearic acid methyl ester, whereafter the mass is worked out to packing materials.

Example 11

10 parts of polymeric vinyl chloride and 10 parts of trans-diacetoxy stearic acid methyl ester are solved in 100 parts of tetrahydrofuran; from this solution may be cast a film of high extensi-

bility and of a resistance to cold of -80° . The solution is suitable for impregnating fabrics and after an addition of 3 parts of pigments it is suitable for producing artificial leather and for covering textile fabrics. Instead of applying methyl ester also butyl ester may be used.

Example 12

100 parts of polymeric vinyl chloride and 100 parts of acetoxy tall oil fatty acid ethyl ester are solved in 500 parts of tetrahydrofurane and 500 parts of methyl propyl ketone. The solution is suitable as a lacquer for cables and yields watertight foils flexible at -35° .

Example 13

100 parts of polymeric vinyl chloride are mixed with 100 parts of cis-diacetoxy stearic acid-3-ethoxybutyl ester and the mass is spattered to elastic plates, hoses, and the like which may easily be welded. They have a resistance to cold of -48° .

Example 14

100 parts of polymeric vinyl chloride and 100 parts of acetoxy chlorostearic acid methyl ester are solved in 800 parts of a low boiling solvent. The solution is suitable for covering metal, glass, paper, and fabrics. The lacquer has a resistance to cold of -39° after removing the volatile constituents.

Example 15

12 parts of polymeric vinyl chloride are kneaded with 4 parts of diacetoxy stearic acid butyl ester and 4 parts of acetoxy chlorostearic acid ethyl ester, whereafter the mass is spattered to elastic and flexible commodities having the resistance to cold of -42° . They may easily be welded.

Example 16

9 parts of polymeric vinyl chloride are melted with 4 parts of chlorinated tall oil fatty acid methyl ester and 2 parts of diacetoxy stearic acid methyl ester, whereby an elastic mass is obtained, having the resistance to cold of -30° and which does not sweat out the softener.

Example 17

3 parts of polyvinyl chloride, 2 parts of diacetoxy stearic acid methyl ester and 1 part of tall oil fatty acid methyl ester are pressed to plates, tubes or foils and thereby products of the resistance to cold of -60° are obtained. After a useful dilution in suitable solvents products are obtained suitable for the covering of electric conducting wires, cables, and the like.

Example 18

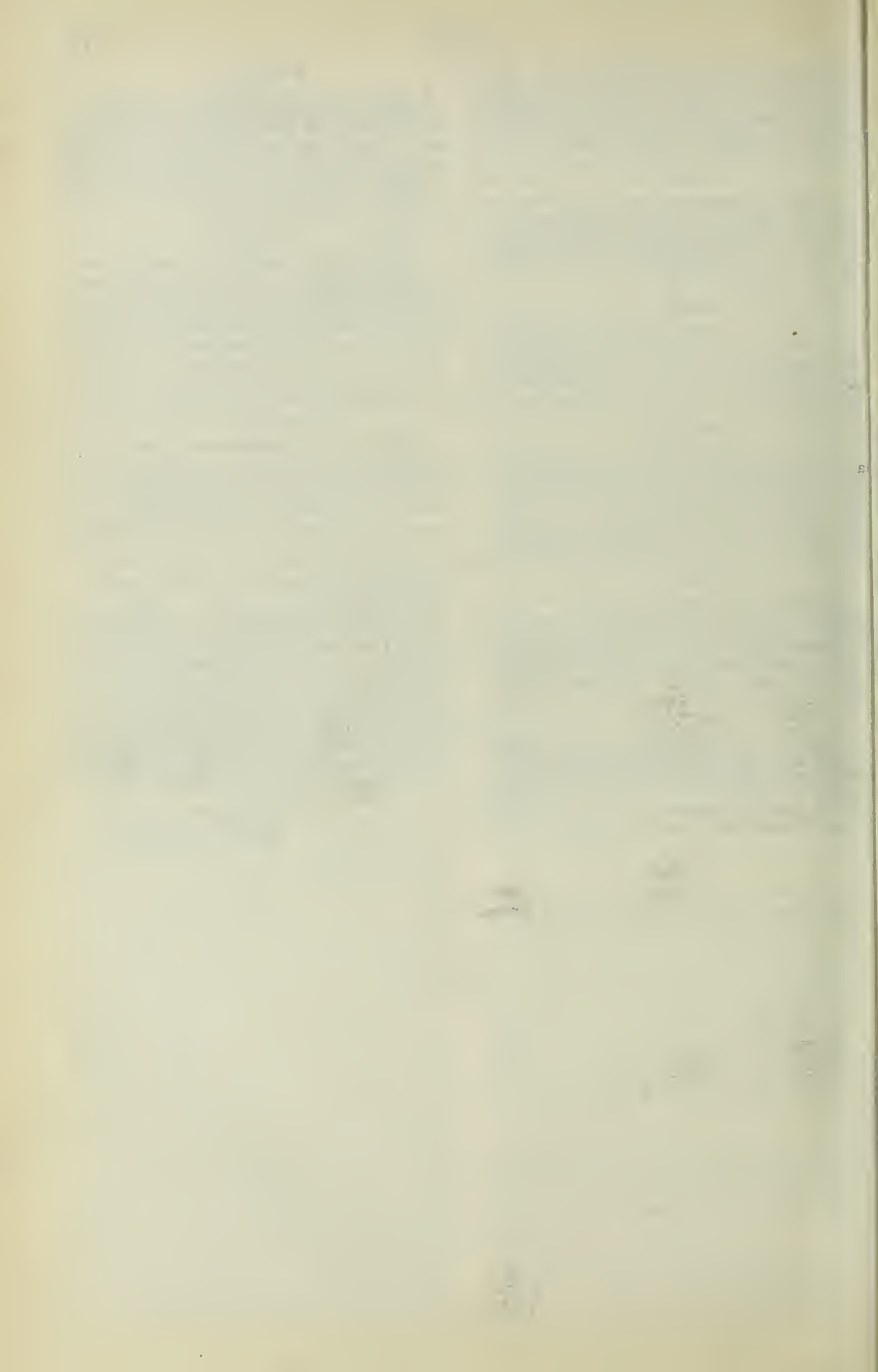
10 parts of acetyl cellulose are solved in 100 parts of methylene chloride-methanol (9:1) and 10 parts of trans-diacetoxy stearic acid methyl ester. The solution may be cast to a flexible film (44μ) which has a resistance to tearing of 2.9 kg pro qmm, 21.3% of extensibility, the bending strength of 281 and the resistance to cold of -70° . The solution is suitable for producing protecting coatings on wood, metal, glass or fabrics.

Example 19

4 parts of cellulose acetate and 4 parts of cis-diacetoxy stearic acid butyl ester are solved in 50 parts of methylene chloride-methanol (9:1) and then the solution is cast to foils. These have (at 61μ) a resistance to tearing of 3.4 kg. pro qmm, 14.5% extensibility, the bending strength of 1900-3000 and the resistance to cold of -80° . The solution is suitable for covering flexible electric conducting wires and cables which are flexible in the cold.

Besides the excellent resistances to cold named above, the high polymeric masses to which the softeners according to the invention are added have also a very satisfying resistance to heat. According to the usual stability test—consisting in heating the mass of artificial material in the nitrogen flow at 170° and in determining the time passed until the first splitting off of hydrogen chloride is identified by a solution of silver nitrate—the masses of artificial material described in the examples 9-19 have resistances to heat of about $2\frac{1}{2}$ hours and more.

WOLFGANG GRUBER.
HANS MACHEMER.



ALIEN PROPERTY CUSTODIAN

ARTIFICIAL MATERIALS AND THE METHODS OF PRODUCING THE SAME

Hans Bergk, Krefeld, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed March 12, 1941

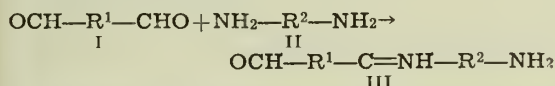
This invention relates to improvements in artificial materials and the methods of producing the same, and more particularly to such materials produced from condensation and polymerization products obtained from dialdehydes and diamines.

An object of this invention is to produce an artificial material in an entirely novel manner.

Another object of this invention is to produce an artificial material having an unusually high resistance to high temperatures.

Still another object of this invention is to produce an artificial material which is practically insoluble in most of the usual solvents.

The methods and products of the present invention is based upon the condensation of dialdehydes and diamines of the type $\text{OCH}-\text{R}^1-\text{CHO}$ and $\text{NH}_2-\text{R}^2-\text{NH}_2$, in which R^1 and R^2 can be bivalent, the same or different aromatic or aliphatic radicals, which may also contain nitrogen, sulphur or oxygen atoms. The condensation product is then further condensed or polymerized to large molecules. The reaction takes place according to the following formula:



wherein III can again react with the same molecules, or molecules of types I or II for the formation of a large molecule chain. The condensation product is condensed or polymerized either immediately or in one or more later steps.

The original substances can be dissolved in a solvent such as alcohol and then brought together for the purposes of the reaction. In this case after some standing a body is precipitated which is practically insoluble in most of the usual solvents. On the other hand, the use of a solvent for the substances is not mandatory, as the reaction will take place instead by the heating of the reaction mixture.

The polymerization itself takes place very easily. It can be accelerated by heating or retarded by cooling, for example at -6°C . In the case of the above method in which alcohol is used as a solvent, the precipitated product may be filtered off therefrom without difficulty. By the addition of heat this filtered off product as well as also the product produced without any solvent may be brought into a plastic condition by raising the temperature. Upon a still further increase in

temperature the substances will again become hard. The final degree of polymerization may be influenced by the addition of such substances which will satisfy the group standing at the end and capable of reaction. Such substances can be, for example, combinations of the type I or type II previously mentioned, or amines, ammonia, aldehyde, acids or acid chloride and similar bodies.

As examples of the foregoing method, and the product which can be obtained, attention is called to the following:

Example 1

A cold-saturated alcoholic solution is made of one molecule of terephthalaldehyde and another of one molecule of phenylenediamine. The two solutions are poured together and subjected to an ice cooling. After a short time a yellow body is precipitated. This body can be easily further polymerized immediately, by heating or by allowing same to stand at normal temperatures or the polymerization or condensation can be delayed by cooling it together with the alcohol to a very low temperature, for example -6°C . This first precipitated product is then held for several weeks. By the use of a higher temperature a further polymerization or condensation is then produced, and in this case the body changes color from yellow to brown. This body has a softening point at a temperature of approximately 200°C ; upon further heating, however, it again becomes firm and is practically insoluble in most of the usual solvents. Furthermore, the body has an extremely high resistance against burning. The body is, however, soluble if cooked for a long time in a concentrated acid or alkali, and will change color from yellow to a bright orange.

Example 2

A second example is identical with example 1, except in this case a molecule of benzidine is used instead of the molecule of phenylenediamine. The body obtained will have the same characteristics as example 1, except that its color will change from yellow to a bright red if cooked in a concentrated acid.

The artificial material produced can be brought into the desired form by the application of heat or pressure or by a mechanical working. It may be then stabilized either by a sudden cooling or by the application of high heat.

HANS BERGK.

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ALIEN PROPERTY CUSTODIAN

POLYCONDENSATION OR POLYMERIZATION PRODUCTS AND METHOD FOR PRODUCING THE SAME

Otto Moldenhauer and Helmuth Bock, Hirschberg/Riesengebirge, Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 12, 1941

This invention relates to improved polycondensation or polymerization products and method for producing the same, and more particularly to such products having hydrazine dicarboxylic acids or their derivatives as a base.

An object of this invention is the production of a novel polycondensation or polymerization product suitable for the formation of artificial fibers.

Another object of the invention is the production of an artificial material from hydrazine dicarboxylic acids or their derivatives.

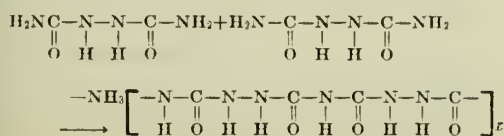
A further object of this invention is the production of an artificial material by the polymerization of hydrazine dicarboxylic acids or their derivatives.

A still further object of this invention is the production of an artificial material by polymerizing the reaction products of hydrazine dicarboxylic acids or their derivatives with derivatives of dicarboxylic acids.

Other objects will be pointed out with more particularity in the description outlined hereinafter.

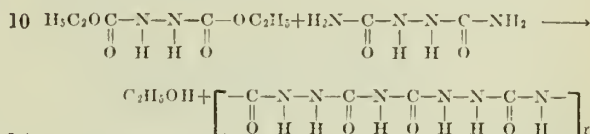
Generally speaking, the subjects matter of the present invention is based upon the discovery that a polymerization product well adapted for the production of fibers and films without the presence of aliphatic or other organic chain members can be produced by the pure or mixed self-condensation of hydrazine carboxylic acids or their derivatives. These derivatives may include not only the esters, chloride and diamides, but also the amidohydrazides and the dihydrazides.

As an example of the foregoing, if one takes hydrazine dicarboxylic acid amide, which may be produced in a known manner either from hydrazine and potassium cyanate or hydrazine and urea, and heats this in a vacuum, a vigorous development of ammonia takes place and simultaneously a viscous melt is produced which permits itself to be further polymerized until it becomes extremely well adapted for the production of fibers. The course of this reaction is substantially as follows:



The invention also contemplates reacting hydrazine dicarboxylic acids with one of its deriva-

tives and polymerizing the reaction product. For example, if an ester of hydrazine dicarboxylic acid is reacted with a further molecule of hydrazine dicarboxylic acid, alcohol is given off and the resulting product may be polymerized to form a melt having strong fiber forming characteristics. This reaction takes place in accordance with the following:



The products so produced show more or less large hydrophilic characteristics which indicates that also hydrazo dicarboxylic acid derivatives can be combined with derivatives of dicarboxylic acids. Accordingly, by the action of hydrazo dicarboxylic amide upon adipinic acid anhydride a condensation product is produced which also has good fiber forming characteristics. Another example of this is shown by the reaction of hydrazo dicarboxylic amide with dicarboxylic amide which, upon the splitting off of ammonia produce condensation products extremely suitable for the production of water-insoluble fibers, films and the like. The course of the reaction is similar to that of the above self-condensation products.

As further examples of the method in accordance with the present invention, there may be suggested the polymerization of an equimolecular mix of hydrazine dicarboxylic acid amide and hydrazine dicarboxylic acid ethyl ester, or an equimolecular mix of hydrazine dicarboxylic acid amide and the anhydride of a dicarboxylic acid, or a mix of hydrazine dicarboxylic acid amide with the amide of a dicarboxylic acid.

In all cases the polymerization is effected by methods in themselves known, including the steps of initiating the polymerization under pressure and ending it without pressure or in a vacuum; the end point of the polymerization can be fixed by the addition of an excess of one of the reaction components either at the beginning or during the course of the reaction, or by a sudden cooling of the reaction mass.

The completed reaction mass is worked into fibers or films in a manner also known to the art, and it is also contemplated that suitable solvents, softening, matting or coloring materials may be added to the reaction mass as desired.

Several specific examples of the methods contemplated by and encompassed within the scope

of the present invention are herewith given by way of example:

Example 1

Fifty-nine parts by weight of hydrazo dicarboxylic amide and one hundred parts by weight of sebacic acid diamide are heated in an autoclave for three hours to 190°C. to 200°C. After this has cooled off a strong ammonia pressure is present within the autoclave. The reaction product is then condensed in a vacuum. After a four-hour heating to 230°C. there is produced a plastic mass which possesses good fiber-forming characteristics and can be molded very easily. It is insoluble in the usual solvents and its softening point lies at 98°C.

Example 2

One hundred parts by weight of hydrazo dicarboxylic amide are heated as quickly as possible in a good vacuum to 290°C. in a reaction chamber provided with a condenser. After the reaction has continued for four hours there will be produced a vitreous product with good plastic characteristics. Urazole produced in slight amounts during the course of the reaction will be found in the condenser.

Example 3

One hundred and eighty-four parts by weight of sebacic acid anhydride are intimately mixed with one hundred and twenty parts by weight of hydrazo dicarboxylic amide and quickly heated to 290°C. When this temperature has been reached the reaction chamber is evacuated and the mass condensed for four hours. The condensation product is bright and transparent and can readily be molded at a temperature of above 165°C.

Example 4

One hundred and eighty parts by weight of hydrazo dicarboxylic acid di-ethyl ester and one hundred and forty-four parts by weight of adipic acid diamide are heated in an autoclave for ten hours to 235°C. in the presence of a slight amount of sodium alcoholate. The alcohol formed is distilled off and the mass condensed for four hours at a pressure of one millimeter of mercury. The condensation product can be very readily molded and is insoluble in the usual solvents.

OTTO MOLDENHAUER.
HELMUTH BOCK.

ALIEN PROPERTY CUSTODIAN

POLYMERIZATION OR POLYCONDENSATION PRODUCT AND THE METHOD FOR PRO- DUCING THE SAME

Otto Moldenhauer and Helmuth Bock, Hirsch-
berg/Riesengebirge, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed March 12, 1941

This invention relates to a Polymerization or polycondensation product and the method for producing the same, and more particularly to such a product which includes a bridge of two or more adjacently lying nitrogen atoms.

An object of this invention is to produce a new type of group of polymerization products which is particularly well adapted for the production of different types of artificial products.

Another object of this invention is the production of a suitable inorganic polymerization product capable of being formed into various artificial products.

Generally speaking, this invention relates to the production of materials of the group including polyhydrazides, polyhydrazones, polymeric azo compounds, polyhydrazo compounds, polyazoxy compounds, and further poly-condensates which must be designated as oxy-hydrazides, polydiazamido compounds and similar classes of compounds as polyhydrazidine.

More specifically, the invention relates to the production of poly-condensation or polymerization products which involve reacting compounds of the di-carbonyl group with hydrazine or its compounds and then polymerizing the reaction product. Since di-carbonyl groups may include, for example, acids such as dicarboxylic acids or their derivatives, especially chloride, anhydrides and esters, and also di-aldehyde and diketone. Dicarboxylic acids will react, for example, with hydrazine to produce hydrazone. The resulting product can be polymerized to form an artificial product capable of forming plastic substances, films, fibers and the like, and, depending upon the final end product desired, may also be supplementarily treated. In this connection, the following supplementary treatments are contemplated:

The polymerized reaction product can be reduced into its corresponding polyazo-compounds; the polymerized reaction product can be hydrogenized into its corresponding polyhydrazido-compounds; the polymerized reaction product can be oxidized into its corresponding polyazoxy-compounds, the polymerized reaction products can be treated with ammonia to produce the corresponding polyhydrazidine.

The actual polymerization step may be varied in various ways known to the art. The polymerization can be effected by the action of raised temperature while the product is subjected to a vacuum. The polymerization can be stabilized at the desired stage by discontinuing the temperature elevation as, for example, by subjecting

the product to a cooling action. The polymerization may be brought to a desired end point by adding an excess of one of the reaction constituents either at the beginning or during the course of the reaction, while an acceleration or delaying action upon the course of the reaction itself or upon the polymerization can be exercised by the addition of foreign materials, such as acids, basis, or salts.

The water or alcohol produced during the reaction can be removed by the use of the principle of the binary or ternary steam mix.

The produced intermediate product can be subjected to the usual dry spinning process either in a fused state with or without the addition of solvents or softening means or can be subjected to a wet spinning process in suitable solvents or thinning material with or without the addition of softening materials and other materials favorably influencing the spinning process. To the intermediate product there also may be added matting means or coloring material in solvent or pigment form before or during the course of the forming.

In mentioning above that di-aldehyde or diketone may be reacted with hydrazine, attention is directed to the fact that bisulphite compounds of such di-aldehydes or diketones are specifically contemplated. Also, while hydrazines have been mentioned, suitable hydrazine hydrates or their salts may also be used.

The following examples will indicate the manner in which the method according to the present invention is effected and the type of product produced thereby:

Example 1

128 parts of adipinic acid anhydride and 50 parts of hydrazine hydrate are brought together. A violent reaction takes place after the conclusion of which the reaction product is heated for five hours to 150° C. The resulting reaction product which is a white body insoluble in the usual solvents is then converted by heating in a vacuum to 290° C. into a high polymeric compound. The polymerization product obtained is capable of being drawn into fibers and can either be spun into threads by means of a constant volume pump through interposed nozzles, or can be shaped by the use of pressure.

Example 2

286 parts of hexadecane dicarboxylic acid is heated with 50 parts of hydrazine hydrate for ten hours with the use of a reflux condenser until complete decomposition takes place. After

the removal of the hydrate-and reaction water, the reaction product is further treated in a vacuum at approximately 200° to 300° C. After approximately three hours of heating one receives a polymerization product which has similar characteristics as in example 1, and which can be treated in a similar manner to produce artificial products or fibers.

The fibers obtained by the methods according to this invention are characterized by extraordinarily high elasticity and strength, and have

such a high fusion point that they are useful with advantage for textile and technical purposes.

While various processes for the production of various artificial material have been heretofore known to the art, it is believed that for the first time there is here disclosed a method for producing what may be termed an inorganic artificial material.

OTTO MOLDENHAUER.
HELMUTH BOCK.

ALIEN PROPERTY CUSTODIAN

POLYMERIZATION OR POLYCONDENSATION PRODUCTS AND METHOD FOR PRODUCING THE SAME

Otto Moldenhauer and Helmuth Bock, Hirschberg/Riesengebirge, Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 12, 1941

This invention relates to improved polymerization or polycondensation products and method for producing the same, and more particularly to such products as are formed from diureids or urea derivatives.

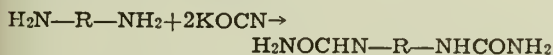
An object of this invention is to produce a new artificial polymerization product suitable for the formation of fibers, films, and the like.

Another object of this invention is the production of a new product derived from the polymerization of urea derivatives.

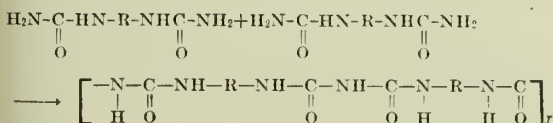
A further object of this invention is the production of a new product derived from the polymerization of diureids.

An additional object is the production of a polymerization product resulting from the polymerization of the reaction product of diureids with organic diamines, dicarboxylic acids or their derivatives.

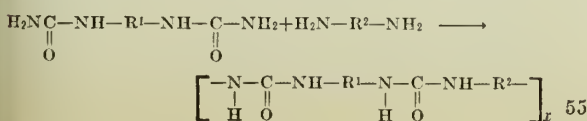
Diureids may be obtained by means of the reaction, known per se, of an organic diamine with cyanic acid or its salts in accordance with the following general formula:



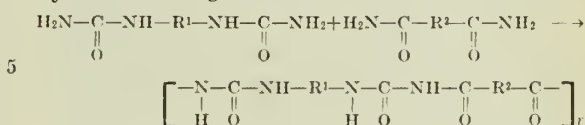
The characteristics of the resulting diureids vary in accordance with the bivalent organic group chosen and represented by "R" in the formula. It has now been found that if one heats this urea derivative in a high vacuum to temperatures above 100°C., self-condensation will take place with a splitting off of ammonia, producing a melt which is extremely well capable of being drawn into fibers. This condensation can be formulated in the following manner:



The reaction takes place in a similar manner if one combines the above mentioned urea derivative with stoichiometrically determined amount of diamines or amides of dicarboxylic acids; in this case the urea derivative shall contain the two urea residues in the α, ω -position. In the first case, the reaction will proceed according to the following:



In the second case the reaction may be indicated by the following formula:



In both cases R^1 and R^2 are the same or different organic groups. Also, in both cases a condensation arises with a splitting off of ammonia and the resulting melt may be used for the production of fibers, films, etc.

Instead of using a diamine or a diamide, a dicarboxylic acid, its esters or anhydrides may be used as the second component. In this event, the reaction proceeds not with a splitting off of ammonia, but with a splitting off of water or alcohol. If anhydrides are used, an even accumulation condensation arises.

In all cases the polymerization can be effected or varied in different ways familiar to the art. The polymerization may take place by the use of raised temperatures in a vacuum. The reaction may be effected under pressure and the by-product arising may be removed in a vacuum. The polymerization may be halted by cooling at the desired stage or brought to a desired end point by the addition of an excess of a reaction component present either from the beginning or added during the course of the reaction.

It is also contemplated that the reaction components be brought together in suitable solvents, depending upon their individual characteristics.

The product obtained by the above-described chemical steps may be treated in various ways known to the art. The polymerized product may be spun directly from the melt or can be first placed in a suitable solution. In the latter case, suitable matting or coloring materials can be added to the solution before the formation of the fibers or films.

In order to more clearly illustrate the principles of the present invention, certain specific examples are given herewith by way of illustration:

Example 1

One hundred parts by weight of tetramethylenediurea, which may be produced in a known manner from tetramethylenediamine hydrochloride with silvercyanate, are heated in the absence of oxygen for two hours at the customary pressure to 260° C. to 270° C. Active ammonia will be released from the melt, which after the end of the reaction is pumped off in a good vacuum. There

is obtained a bright condensation product having a softening point of 196° C., which is well adapted for working into fibers or films. This is insoluble in the usual solvents.

Example 2

Seventy-five parts by weight of ethylenediurea are heated with one hundred and one parts by weight of sebacic acid and two hundred parts by weight of water for five hours under pressure to 190° C. At the end of the reaction the water is distilled off and the reaction product polymerized by a four hour heating in a vacuum. There is obtained a vitreous mass having very good molding characteristics.

Example 3

One hundred parts by weight of octamethylenediurea are heated for four hours to 280° C. in the absence of oxygen. After this time the reaction vessel is then well evacuated and heated again for another hour. There results a condensation product having a softening point of 218° C. The resulting fibers and films have good elastic properties.

OTTO MOLDENHAUER.
HELMUTH BOCK.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR ISOLATING PENTAERYTHRIT FROM ITS SOLUTIONS

Auguste Florentin Bidaud, Serezin-du-Rhone, Isere, France; vested in the Alien Property Custodian

No Drawing. Application filed March 12, 1941

The present invention relates to a process for obtaining pure pentaerythrite from its impure solutions and more particularly from impure solutions arising from its manufacture.

Pentaerythrite is industrially prepared by condensing acetaldehyde and formol in an aqueous medium in presence of a condensating agent. As is known, the reaction between these two aldehydes does not take place solely in the desired direction; secondary reactions always occur simultaneously, giving rise to other substances, in particular to dipentaerythrite, so that, at the end of the condensation, an aqueous solution of pentaerythrite containing various impurities is obtained. For separating pentaerythrite therefrom, the known processes consist in more or less highly concentrating the solution, after having eventually freed it from the condensating agent, and in allowing the concentrated solution to cool, for causing the crystallization of the pentaerythrite which is separated in the cold state.

The product obtained by this method of procedure always contains certain impurities such as dipentaerythrite, which crystallize with the pentaerythrite and which it is consequently very difficult and sometimes impossible to separate completely by recrystallization. For certain raw products, recrystallization does not even allow of obtaining an improvement in the quality.

According to another proposed technique, the raw solution is concentrated under vacuum at 35° until a content in dry substance of 70 to 75% is obtained, the solid product being then filtered or dried in the cold state. The Applicant has found that this technique offers no advantage over the preceding one as regards the quality of the product.

The difficulties, arising from the fact that certain impurities crystallize at the same time as the pentaerythrite, are well known to those skilled in the art and are mentioned in particular in the French Patent No. 786,909 dated February 14, 1935. For taking advantage of the impure raw product, said patent proposes to free it from the impurities which defile it, by a special washing process with friction.

The Applicant has found, and this is what forms the subject-matter of the present invention, that, contrarily to what was known up to now, it is possible to directly obtain by crystallization, pentaerythrite of great purity giving, in particular, in the cold state, clear aqueous solutions. It suffices, and it is essential for obtaining this result, to effect the crystallization and separa-

tion of the pentaerythrite at a temperature higher than 40°, that is to say at 45°, 80°, 100°, and even more. At these temperatures, the impurities and, in particular, dipentaerythrite, remain dissolved in the mother-water, which is not the case when the operation is effected at lower temperatures. Pentaerythrite is thus obtained which is practically free from accessory products. The temperature at which the process is carried out, for the crystallization itself as well as for the separation of the crystals, can be chosen in the conditions above defined, in particular according to the nature of the solutions treated or the facilities of execution.

A particularly advantageous method of carrying out the invention consists in causing crystallization by concentrating the solution in the hot state. In proportion as evaporation takes place, the pentaerythrite crystals deposit and their quality remains excellent, even if the concentration is continued until nearly the totality of the pentaerythrite contained in the mother-solution is separated. Thus, in a single operation, a very high output of a practically pure product is obtained.

Another particularly advantageous method of procedure for treating crystallizing mother-waters or washing waters and more generally solutions of low pentaerythrite content, consists in concentrating the solution at a high temperature, then in slightly cooling and in separating the pentaerythrite crystals deposited during the cooling; said crystals constitute a product of good purity, if they are separated at a high temperature according to the invention.

Example 1.—Condensation is effected between the acetaldehyde and the formol (4,6 molecules for 1 of acetaldehyde) in presence of lime (0,6 molecule for 1 of acetaldehyde). The lime is eliminated from the reactive liquid by treating with oxalic acid. After filtration, an impure solution is obtained containing about 10% of pentaerythrite.

100 parts of this solution are concentrated under vacuum at 85° until 84 parts of water are distilled. The crystals formed are separated from the mother-waters by draining at this same temperature, washed with a small quantity of a saturated aqueous solution of pentaerythrite, and dried. 90% of the pentaerythrite present in the initial solution is thus extracted. This very pure product gives a clear solution in cold water. Its melting point according to the Maquenne block is 262°.

If the concentration of the same solution is effected at 35° instead of 85°, the product ob-

tained is impure, even if the concentration is carried much less far. Its melting point according to the Maquenne block only reaches 242° and it gives a very turbid aqueous solution.

Example 2.—A commercial pentaerythrite giving in the cold state a turbid aqueous solution and melting at 235 to 246° (melting point taken in a capillary tube by gradually raising the temperature), is dissolved in 3 parts of boiling water. The filtered solution is concentrated when boiling at an ordinary pressure, at about 104° , with stirring, so as to eliminate 2,5 parts of water. The concentration being terminated, cool-

ing is effected, whilst continuing the stirring, to a temperature of 90° ; the crystals (0,9 part) are separated at this temperature, washed and dried. Pure pentaerythrite is thus obtained giving a clear solution in an excess of cold water and the melting point of which, determined in a capillary tube in the same conditions as for the initial product, is from 253 to 255° . By evaporating the mother-water in the dry state with care, 0,1 part of very impure pentaerythrite is extracted, giving in the cold state an extremely turbid aqueous solution.

AUGUSTE FLORENTIN BIDAUD.

ALIEN PROPERTY CUSTODIAN

POLYMERIZATION OF BITUMEN

Franz Hendgen, Selters, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed March 12, 1941

The present invention concerns a process, by which the field of employment of bitumen is enlarged.

Owing to their chemical and physical qualities bitumen and alike products, such as asphalts and pitches, hitherto could only be employed for certain industrial purposes. One has tried to improve them by chemical transformations and thus enlarge their field of employment. Except for oxidation and sulphurizing these experiments, however, were unsuccessful. Although the bitumina were improved in physical respect, by taking up oxygen (blowing) or supplying with sulphur, this would not enable them to be employed for more and useful purposes. Sometimes this oxidation or sulphurizing has been called "polymerization" of bitumen. There is, however, no doubt about this "polymerization" not being a real polymerization. What is to be observed are only oxidation or dehydrogenation processes. The characteristic molecular enlargement, which takes place in the case of a true polymerization, is missing. This follows plainly from the comparison of the coefficients of viscosity of blown or sulphur containing bitumen on the one hand and normally distilled products on the other hand.

According to the present invention it has been found that mineral oil bitumina, tar pitches and such like products under certain conditions may be polymerized, if polymerized together with one or more compounds, which are polymerizable in themselves. By this so-called heteropolymerization products with new and specific qualities are obtained. Bitumen, may, for example, be polymerized together with vinylic derivatives, acrylic acid or its derivatives, as well as with dien com-

pounds, such as butadiene, isoprene, as well as their derivatives, with or without a polymerization accelerator. The fact that the resulting products neither show a bitumeneous character nor the qualities of the pure polymerics of the second compound taking part in polymerization gives a proof of this process being a real polymerization. According to the components products are obtained, the chemical and physical properties of which are different from those of bitumen or the polymerics of the second compound taking part in reaction. All products show a considerably increased viscosity so that one came to the conclusion that they are of long-chained macromolecular structure. In many cases the final products are of utter resistancy against chemical influences. For example the heteropolymeric obtained from bitumen and monomeric chloroprene withstands both 60% sulfuric acid and concentrated nitric acid. Some of the products solve under conditions different from those under which pure bitumen on the one hand and the pure polymerics on the other hand do solve. For example the heteropolymeric from bitumen and monoacrylic methylester solves completely in acetone.

All these observations show that obviously the described reactions are true polymerizations, the olefin bonds existing in the bitumen probably representing the preliminary condition, under which the chain polymerization may form. This opinion is being supported by the fact that, as has been observed, it is much more difficult to polymerize blown bitumina than distilled bitumina.

FRANZ HENDGEN.

THE HISTORY OF THE

PROVINCE OF NEW HAMPSHIRE

FROM THE FIRST SETTLEMENT TO THE PRESENT TIME

BY SAMUEL JOHNSON

IN TWO VOLUMES

LONDON: PRINTED BY J. JOHNSON, ST. PAULS CHURCH-YARD

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ALIEN PROPERTY CUSTODIAN

POLYAMIDES

Kurt Thinius, Eilenburg, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed March 13, 1941

My present invention relates to polyamides and more particularly to polyamides containing plasticizers.

Fibers, filaments, films, plastic articles, artificial leather and the like may also be produced in different ways from polyamides, i. e. synthetic polymerized condensation products having the recurring atom grouping —NH—CO— . In order to render these molded articles suitable for various purposes it is convenient to use softening agents in the production thereof. The addition of the usually employed esters of polybasic inorganic or organic acids with aliphatic or aromatic alcohols or phenols in the working up of polyamides has, however, proved without success. Provided that the polyamides and these known substances are compatible with each other, the small amount thereof which can be added, only unessentially influences the properties of the polyamide, for instance, of polyamide foils, in the desired direction. This object could surely be accomplished by the employment of polyhydric alcohols as plasticizers. However, these compounds have the disadvantage not to be water-insoluble. It is noted that both classes belong to the group of non-gelatinizing plasticizers. The working up of the polyamides, however, necessitates the presence of a gelatinizing softening agent in many cases.

The present invention is based on the observation that 3-chloropropyleneglycol-(2)-phenylether-(1) is a plasticizer for polyamide which is not only compatible with polyamides in any proportion but also insoluble in water. Moreover this chloroether is capable of dissolving to a certain extent interpolyamides as, for instance, prepared from adipic acid, hexamethylene-diamine, and caprolactam already at ordinary temperature. On heating the polymers from these reactants completely dissolve in this softening agent. The chloroether of the invention is a viscous liquid clear as water and soluble in the usual organic solvents. It meets the requirements as for volatility, fastness to light and resistance to cold and heat. It is furthermore of advantage that the chloroether can be worked up together with every pigment since it is free from acid. Finally the new plasticizer possesses the property to increase the compatibility of the polyamides with the substances hitherto used as softening agents.

The following Examples illustrate the invention:

Example I

20 g of 3-chloropropyleneglycol-(2)-phenylether-(1) are added to a solution consisting of 80 g of an interpolyamide from hexamethylenediamine adipate and caprolactam, 216 g of a mixture of methanol (80%) and methylenechloride (1:1), 40 g of ethylenechlorohydrine and 8 g of butanol. On casting the solution forms a pliable polyamide film which is preferably suited to wrapping material and the like. The solution may also be used as a lacquer or adhesive.

Example II

80 g of 3-chloropropyleneglycol-(2)-phenylether-(1) is mixed with the interpolyamide solution described in Example I. The solution thus obtained is then cast to form a film. This film is capable of adhering to glass plates especially strongly and is, therefore, preferably suitable for the production of compound glass. With an addition of pigments such films may also be used as leather substitutes.

Example III

A pasty mass is prepared by mixing about equal amounts of a finely powdered polyamide and 3-chloropropyleneglycol-(2)-phenylether-(1). The paste is applied to an absorptive support of any structure and composition. The paste is gelatinized at elevated temperature and one thus obtains a water-proof coating on the support having a soft and flexible touch. By additions of filling agents, pigments and/or other substances products like artificial leather the surface of which may be modified by a pressure treatment together with or subsequent to a gelatinizing procedure can be obtained in this convenient manner. If desired, the pasty mixture may also be produced and used with an addition of organic liquids capable of dissolving or swelling the polyamide and/or the plasticizer. Finally especially thinly liquid compositions can be prepared by mixing the polyamide with an aqueous emulsion of the plasticizer.

KURT THINIUS.

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ALIEN PROPERTY CUSTODIAN

RESINOUS CONDENSATION PRODUCTS AND PROCESS OF MAKING THEM

Herbert Hönel, Vienna, and Alois Zinke, Graz,
Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 24, 1941

The invention relates to condensation products formed by the reaction of high molecular terpene phenols, with formaldehyde, which condensation products may be used for the preparation of varnishes.

The present application is a continuation in part of our application Serial No. 141,554, filed May 8, 1937 which in turn is a division of our application Serial No. 30,152 filed July 6, 1935, now patent No. 2,123,898 dated July 19, 1933. In the latter are claimed some of those terpene phenols which are employed for the preparation of the condensation products claimed in application Serial No. 141,554 and in the present application.

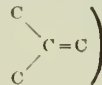
In our application Serial No. 141,554 is claimed a process which comprises condensing together in the presence of a condensing agent capable of eliminating hydrogen halide (1) a poly-halogenated terpene and (2) a phenol in the proportion of substantially more than one molar weight of the phenol to each molar weight of the poly-halogenated terpene whereby substitution of the halogen atoms by phenolic aromatic radicals takes place with elimination of hydrogen halide, continuing the condensing action at elevated temperature until a condensation product is obtained consisting essentially of the terpene and the phenol in chemical combination in substantially the aforeside proportion and then condensing the said condensation product with an aldehyde. The present application relates to a process of producing resinous phenol formaldehyde condensation products, which comprises subjecting a terpene phenol condensation product which has at least one double bond and which is derived from a terpene and a phenol in the proportion of more than one molar weight of the terpene to each molar weight of the phenol, to a prolonged heat treatment in the presence of a metal halide of the Friedl-Crafts type and hydrogen halide until a solid resin is obtained and condensing the said resin with formaldehyde.

In carrying out the process of our invention we start from the following materials: 1) Terpenes which easily form poly-halogen compounds, preferably by addition of hydrogen chloride, 2) phenols such as common phenol or its easily available homologues, 3) formaldehyde or its polymers or homologues.

The term terpene will be used in the following description and claims for terpenes in the restricted sense of the term such as limonene, terpinolene, terpene, terpineol, carvone, etc.; sesquiterpenes such as cadinene; polyterpenes such as

coniferyl alcohol; acyclic compounds which readily derive from or may readily be converted into terpenes, such as the so called "terpenogenes" or "olefinic terpenes" e. g. isoprene, geraniol, linalool, terpinehydrate, citral; compounds of undefined constitution e. g. deriving from polyterpenes mainly by means of heat treatments or other simple chemical conversions; in many cases these substances constitute cheap waste products.

These compounds are characterised in that they readily form poly-halogen compounds. Unsaturated compounds in which a tertiary carbon atom is connected by a double linkage with another C atom (as illustrated by the grouping



are particularly suitable since they form tertiary halogen compounds (halides) by mere addition.

There are many easily available materials which at least contain a high percentage of such chemically strictly determined terpenes as mentioned above. We wish to mention dipentenenes, conifer oils, pine oil, cuminoil (caraway seed oil), various decomposition (depolymerisation)—products of rubber and natural resins such as rosin oil, copal oil.

According to our invention one or more members of the first group briefly referred to as terpenes are chemically combined with one or more members of the second group by producing halogen compounds, such as by addition or other interaction from suitable terpene compounds and hydrogen halides and causing these products to react with the members of the second group i. e. the phenols in the presence of aluminum chloride, zinc chloride, ferric chloride or other suitable metal halides or substances which form the same under the conditions of the reaction, such as zinc or iron dust.

For our preferred process we either first prepare the hydrogen halide addition or conversion products separately or in the presence of the phenol, or we form them immediately by means of the hydrogen halides set free during the condensation. Hydrogen halide which has been set free by reacting the phenol with any other suitable organic halogen compound, such as a tertiary alkyl halide or benzyl chloride or the like, may also be used for this intermediate formation. In this case the aforeside organic halogen compounds serve as additional auxiliary material for initiating the condensation between the phenol and the terpene-like compound.

The last mentioned method of forming hydrogen halide addition or conversion products in the presence of phenols, is limited to terpene-like compounds which in the course of the reaction of the hydrogen halide do not form water, such as would render the catalyst inactive or at least would have a very detrimental effect thereon.

For the sake of completeness we wish to mention that in some cases (which, as stated above, are restricted to non-alcoholic terpenes) the condensation reaction may be performed by means of aluminum chloride, or the like, alone. The hydrogen halide necessary in initiating the condensation reaction, is formed from the aluminum chloride since traces of water are generally present.

By employing relatively small quantities of the phenol particularly when condensing during a relatively short time and when employing small quantities of the catalyst as a rule soft or even only viscous terpene phenols are obtained. Unexpectedly we have found that even those soft condensation products can be converted into resinous solid products, obviously in virtue of their unsaturated character or their capability of forming a double linkage under the prevailing conditions. This conversion probably is caused by polymerisation; we effect it by heating the condensation product for a particularly long period, preferably in the presence of a comparatively large quantity of catalysts. As suitable catalysts there are to be regarded metal halides of the Friedl-Crafts type in conjunction with hydrogen halide which may be introduced into the reaction mixture or is formed during the condensation. Products may be obtained which have a by far increased molecular size and which, notwithstanding a relatively small proportion of combined phenol, indicate the presence of several phenolic benzene nuclei in the molecule. They behave very similarly to terpene-phenols which are obtained from polyvalent terpene halides and phenol in excess, and which themselves are to be regarded as polyvalent polynuclear phenolic compounds.

The hereinbefore described method of carrying out our process is particularly advantageous because in this way it is also possible to compound practically all the phenol. Otherwise uncombined phenol as a rule remains behind and must be removed by washing or by steam or vacuum distillation.

The terpene phenol compounds are then subjected to condensation with formaldehyde. Condensation products of particular technical value may be obtained showing the most various properties. These depend on the proportions, the catalyst, temperature and duration of the reaction and on other controllable conditions. The variability is far broader than otherwise known when condensing phenols with aldehydes.

In order to facilitate the mutual contact between the high molecular phenols and the aqueous formaldehyde, we prefer to employ as auxiliary materials indifferent solvents, such as saturated or aromatic hydrocarbons or alcohols, which may be removed after condensation has taken place. It is particularly advantageous to condense the high molecular phenols with formaldehyde in a manner known per se at ordinary or only moderately elevated temperatures for a prolonged period of time by means of a strong alkali and subsequent neutralization. By means of this process we obtain formaldehyde condensation products showing a considerable harden-

ing character if condensing high molecular phenols obtained from common phenol although they have combined only a relatively small proportion of phenol. We even concluded from the distinct hardening character peculiar to these formaldehyde condensation products, that the solid resinous phenolic body contains several hydroxyphenyl groups in the molecule i. e. that a polyphenylol-terpene compound is formed. In contradistinction thereto the still oily or soft interaction product primarily obtained from phenol and e. g. dipentene in the proportions mentioned above, even when condensed with formaldehyde according to our particular condensation process, leads to products having little or no hardening capacity. The maximum amount of formaldehyde which can be compounded is dependent on the quantity and on the constitution of the phenol employed for producing the high molecular terpene phenol. E. g. terpene phenols obtained from o-cresol or technical mixtures of cresols, xylenols etc. and dipentene exhibit only a very poor or no hardening capacity.

Condensation products deriving from the last mentioned phenols, also when obtained according to our particular condensation process, are easily compatible with all kinds of varnish raw materials such as resins and fatty oils of the drying or non-drying type. If however phenol is used as starting material the resulting terpene polyphenylol compound may form an oil incompatible heat hardening formaldehyde condensation product unless certain precautions are taken. We either reduce the proportion of formaldehyde below the maximum quantity which can be taken up, to a sufficient extent or we employ polyphenylol compounds in which the terpenic part is particularly large.

However it is also possible and in some cases advantageous to achieve oil compatibility only by a secondary treatment of an oil incompatible heat hardening condensation product. A preferred treatment consists of simply heating this condensation product with an alcohol for some time at elevated temperature until the desired compatibility is achieved. The presence of a slight amount of an acid accelerates such modification. An other way which secures sufficient oil compatibility consists in the coemployment of phenols such as p-tert.-butyl phenol, amyl phenol etc. which, when used alone, lead to completely oilsoluble condensation products due to their reduced activity and long chain substituents.

It is remarkable that the formaldehyde condensation products of the oil reactive type derived from some of our polyphenylol compounds, despite the particularly large terpenic substituent, exhibit a greater hardening capacity than e.g. products of this type derived from ordinary alkyl phenols such as p-tert.-butyl phenol; this can be seen from the greater increase in viscosity of the oil-resin reaction mixture.

The new resins represent excellent basic materials for varnishes both of the air and stove drying type. Their employment in oil varnishes remarkably increases the resistance against water and weathering conditions. A particular advantage of these resins insofar they belong to the oil reactive type, consists in that they do not disturb the drying capacity of the oil they are reacted with, in contradistinction to oil reactive resins obtained from alkyl phenols. Excellent results may also be obtained when combining or interacting resins prepared according to our in-

vention with resins, particularly of the drying alkyd type.

The following examples may serve for illustration. We wish it to be understood positively that they are not restrictive as to the proportions etc. used.

Example 1

100 parts of phenol and 250 parts of technical dipentene of which a small part was first saturated separately or in the presence of the phenol, with hydrogen chloride, are condensed at 50–70°C. in the presence of 3 parts of zinc chloride.

If the reaction mixture is subjected after a few hours to steam distillation, about 250–255 gms. of a soft or viscous residue are obtained. If heating is continued for a further 48–72 hours, preferably at somewhat higher temperatures, and after increasing the catalyst, about 320 gms. of a residue remain after steam distillation in the form of a solid resin. About 15 gms. of inactive fractions of the technical dipentene and hardly any unused phenol pass over with the steam. The solid resinous condensation product has far higher molecular weight than the soft or viscous one primarily obtained. It is noticeable that far more than one mol. of the terpene per each mol. of phenol has been combined.

A heat hardening oil soluble resin e.g. is obtained when condensing this product which is considered to be a polyphenylol compound, with a large polyterpene substituent, with about 200 parts of formaldehyde (40% vol.). This step is performed by first diluting the resinous phenylol compound in a small proportion of an inert solvent such as toluene or xylene and adding caustic soda solution until a homogeneous reaction

mixture is obtained. After several days the mixture is neutralized and the resin solution obtained thoroughly washed. After evaporating the solvent a resin is obtained which shows a very distinct hardening capacity. Its compatibility with neutral varnish materials including drying oils is surprising, for the phenolic body from which it derives at least mainly consists of a polyphenylol terpene having more than two unoccupied reaction favorable positions.

Example 2

If reducing the dipentene to about 170 parts per 100 parts of phenol and operating in the same way as in Example 1 a solid resinous phenolic compound is obtained in which approximately equimolecular quantities of phenol and dipentene are chemically combined the formaldehyde condensation product prepared in the same way and with the proportion as in Example 1, exhibits such an intense hardening capacity that no homogeneous interaction products can be obtained with neutral resins or oils.

It can be rendered oil soluble by heating it with about 100 parts of ordinary alcohol in the presence of a slight quantity of hydro chloric or phosphoric acid at about 60–80°C. for several hours.

It is very noticeable that the still viscous interaction product primarily obtained by only a short interaction of phenol and dipentene in the same proportions, does not lead by any means to formaldehyde condensation products of any pronounced hardening capacity.

HERBERT HÖNEL.
ALOIS ZINKE.

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF ALIPHATIC ACIDS

Henri Martin Guinot, Niort, France; vested in the
Alien Property Custodian

Application filed March 24, 1941

It is known to oxidise acetaldehyde, previously diluted with acetic acid, by means of a current of air or inert gases containing oxygen in more or less considerable quantity. The reaction is generally activated by catalysts, such as salts of manganese, cobalt, copper, cerium and the like.

The operation is mostly carried on in a continuous way, aldehyde being caused to arrive simultaneously with the gas containing oxygen into a reaction vessel provided with stirring means for finely emulsifying such gas and the liquid under treatment.

Generally, the products obtained from the oxidation of aldehyde are separated by distillation from the liquid which is caused to escape by overflow of the reaction vessel into which the air or gas of reaction and aldehyde to oxidise are introduced.

This way of operating presents inconveniences which consist in withdrawing from the reaction medium a certain quantity of catalyst and complicating the distillation by reason of residual deposits formed in the evaporation system and containing peroxidised derivatives which deteriorate metals forming such system.

The present invention has for its object a process which permits not only avoiding the inconveniences referred to, but also improving operative yields hitherto generally obtained.

The invention essentially consists in carrying the acid manufactured in the reaction vessel with a current of gas circulating between this vessel and a well cooled condenser. The intensity of the gaseous current is adjusted in such manner as to cause the quantity of acid carried therewith and condensed to correspond to the quantity manufactured. In this way the volume of the liquid within the reaction vessel remains substantially constant, and the catalyst is not carried away from the vessel, whereby its proportion may be increased to attain the favorable effect desired and the catalyst introduced may last indefinitely.

The condensed product is then separated down to its elements and dehydrated by distillation, eventually in accordance with the principles of azeotropic distillation.

It is also known to be advantageous to effect the reaction of oxidation of acetaldehyde diluted with acetic acid by operating at a moderate temperature, for example between 30 and 60° centigrade. Above such temperature the quantity of carbon dioxide formed by the combustion of acetaldehyde will increase very rapidly and the respective yields will decrease.

When the operation is carried on at such temperature a current of air containing oxygen necessary to the oxidation of aldehyde is not capable of carrying away with it the quantity of acetic acid vapours corresponding to that which has been formed. It is for this reason that, according to the present invention, the gaseous mixture grown poor in oxygen and having been deprived of products of the oxidising reaction is caused to circulate in the vessel of reaction. In this way there is brought about the complete removal of acetic acid formed by the oxidation of acetaldehyde in the bath.

The process of this invention is also utilisable in the case of aliphatic aldehydes containing more than 2 carbon atoms in the molecule.

In order to show how the invention may readily be carried into practical effect, the following examples are given for the purpose of illustration, but not of limitation, with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a plant for the manufacture of acetic acid according to the invention, and

Figure 2 is a schematic representation of a plant for the manufacture of propionic acid according to the invention.

EXAMPLE I.—*Manufacture of acetic acid.*

1 metric ton of crystallizable acetic acid containing 25 kgs of acetaldehyde and 1 kg. of acetate of manganese is introduced into a reaction vessel 1 (Fig. 1) provided with a pipe coil 2 for heating or cooling and a turbine member 3 for finely emulsifying the gas and liquid within the vessel 1. The liquid in the latter is heated by means of the coil 2 to the temperature of 60° Centigrade and then there are introduced into the liquid through a pipe 4 a current of air at the rate of 270 cubic meters per hour and through a pipe 5 acetaldehyde at the rate of 150 kgs per hour. The reaction of oxidation sets in and soon it becomes necessary to cool by introducing cold water into the coil 2 in order to maintain the temperature within the vessel 1 at about 50°C.

Hot gases leaving the oxidiser 1 through a conduit 6 are cooled in a condenser 7 at the outlet end of which gases grown poor in oxygen and separated in a separation head 10 are taken up by a fan or blower 8 by which they are blown through a conduit 9 back into the reaction vessel 1. The blower 8 is so adjusted as to discharge 800 cubic meters per hour, such discharge being sufficient to extract out all of acid formed in the reaction at the temperature of 50°C.

In the separation head 10 the condensed liquid, which is constituted by a mixture of

	Per cent
Acetic acid-----	97
Acetaldehyde-----	2
Water-----	1

is separated from the poor gases taken up by the blower 8 and flows thereout through a pipe 11 at the rate of 135 kgs per hour.

This liquid is introduced into the median portion of a distillation column 12 ahead of which through a pipe 17 there is withdrawn acetaldehyde which is reintroduced into the reaction vessel 1. At the base of said column there flows out through a pipe 13 hydrated acetic acid at a concentration of about 98% which is then dehydrated azeotropically in a second distillation column 25 once for all charged with a suitable quantity of a carrier such as ethyl acetate.

The azeotropic mixture ethyl-acetate-water, after condensation at 26, is decanted at 28. The aqueous layer is drawn off, while the upper layer mainly constituted by ethyl acetate is continuously returned through a pipe 27 to the top portion of the column 25. At the base of the latter there is collected at 29 anhydrous acetic acid.

The total efficiency of the oxidation is 98.6%.

Through a pipe 24 connected with the discharge end of the blower 8 flows off a gas including still 5 to 6% of oxygen, from which acetaldehyde and acetic acid vapours contained therein are removed by simple washing or by other known means.

EXAMPLE II.—*Manufacture of propionic acid*

The reaction vessel 1 (Fig. 2) is charged with

1000 kgs of propionic acid containing 50 kgs of propionaldehyde and 5 kgs of propionate of manganese.

The mixture being heated up to 75° C., there is introduced into the vessel 1, on one part, propionaldehyde at the rate of 125 kgs per hour and, on the other part, an air current at the rate of 200 cubic meters per hour.

As soon as the reaction sets in, the temperature of the liquid mixture in vessel 1 is adjusted to 60° C. and the formed products are caused to be eliminated by means of the gaseous current produced by the blower 8 which is adjusted to discharge 750 cubic meters per hour.

The product condensed at 7 and constituted by propionic acid including propionaldehyde and a small quantity of water is introduced into a distillation column 12 at the base of which there is collected at 13 anhydrous propionic acid.

At the top of column 12 through a pipe 14 escapes a mixture of propionaldehyde, water and propionic acid, which mixture is condensed at 15 and partially returned through a pipe 16 to the top portion of column 12. The remainder of this condensation is introduced through a pipe 17 into the median portion of a distillation column 18 at the base of which there is collected at 19 anhydrous propionic acid, while ahead of this column at 22 is drawn off a mixture of propionaldehyde and water, which is separated by known means down to its elements, propionaldehyde being reintroduced into the reaction vessel 1.

The total efficiency of the oxidation is 98.7%.

HENRI MARTIN GUINOT.

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APRIL 20, 1943.
BY A. P. C.

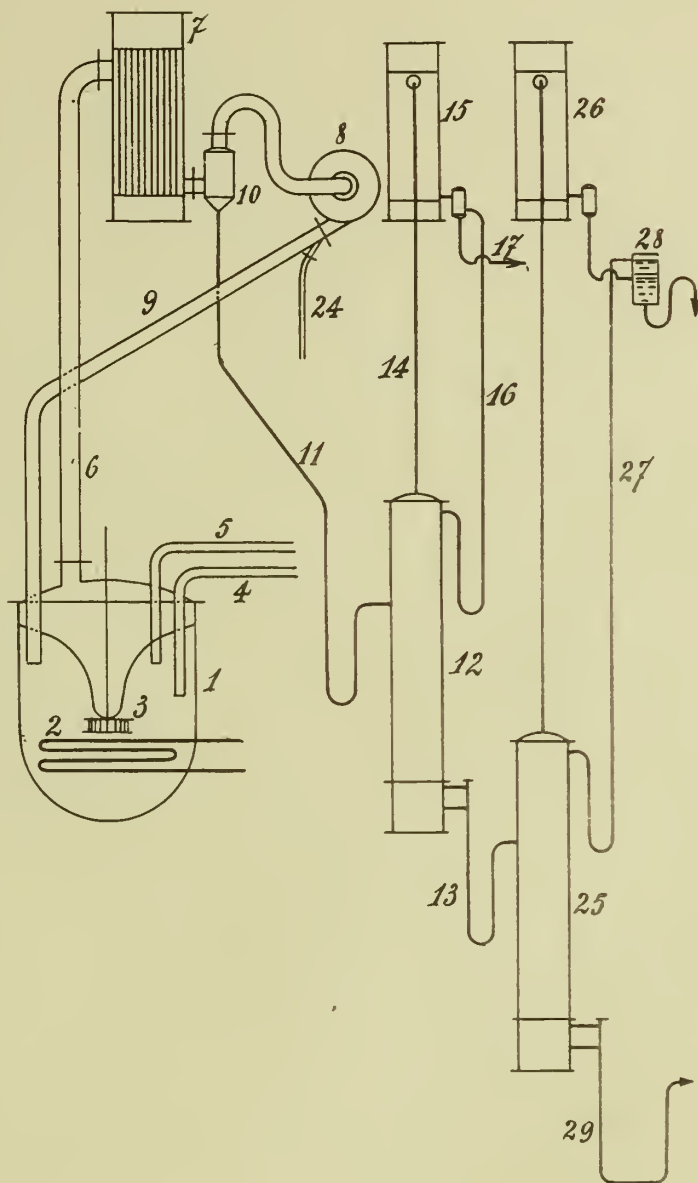
H. M. GUINOT
MANUFACTURE OF ALIPHATIC ACIDS

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2 Sheets-Sheet 1

Fig. 1.



Inventor
HENRI M. GUINOT

By Richard K. Stevens

Attorney



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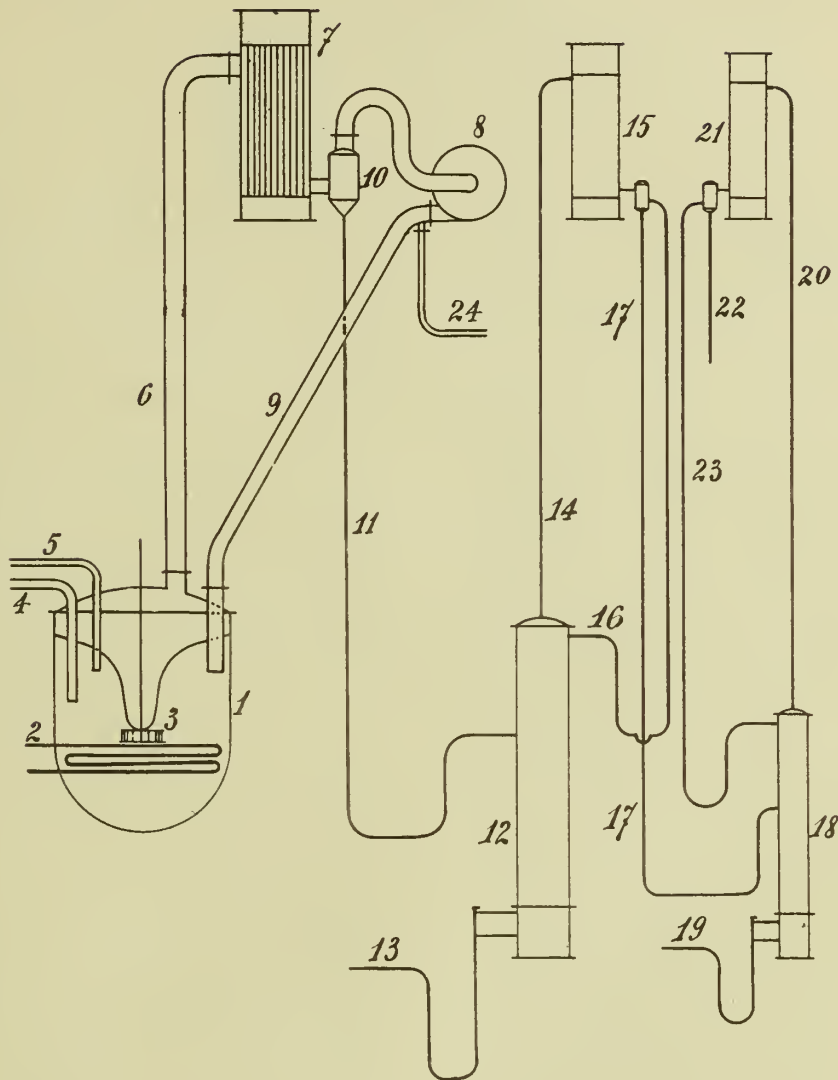
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2 Sheets-Sheet 2

Fig. 2



Inventor
Henri M. Guinot

By Richard K. Stevens

Attorney



ALIEN PROPERTY CUSTODIAN

PROCESS FOR PREPARING CAPILLARY ACTIVE SUBSTANCES

Winfrid Hentrich, Rodleben B. Dessau-Rosslau,
Erik Schirm and Heinz-Joachim Engelbrecht,
Dessau, Germany; vested in the Alien Property
Custodian

No Drawing. Application filed March 26, 1941

This invention relates to capillary active substances and to a process for their preparation. More particularly it relates to a process for preparing capillary active substances from sulfimides which have besides the imide group at least one group having at least one easily exchangeable hydrogen atom or metal atom respectively linked to a hetero atom or a hetero atom group and compounds, which have in the molecule besides a lipophile group an easily exchangeable halogen atom.

It is an object of this invention to provide the soap, laundry, textile, leather, fur, paper and the like industries with capillary active substances which are readily convertible into water soluble soap like salts and have excellent foaming, washing and cleaning properties.

In the co-pending application of Winfrid Hentrich and Erik Schirm filed August 3, 1939, Ser. No. 238 130 there is described a process for preparing capillary active substances constituted according to the general formula



wherein at least one of the two substituents R and R' stands for an organic radical containing at least one lipophile group, which may be interrupted by hetero atoms or hetero atom groups, whereas the other radical may be any hydrocarbon radical eventually interrupted by hetero atoms or hetero atom groups, and Kat denotes any desirable kation which is capable of forming water soluble salts. The process consists in condensing sulfonic acid halogenides of the general formula $R-SO_2-Hal$ with sulfonic acid amides of the general formula $R'-SO_2-NH_2$ or its suitable metal derivatives respectively and in converting the obtained condensation products with inorganic or organic bases into water soluble salts.

In accordance with the present invention it has been found, that in cases, where the lipophile groups of the above denoted compounds are interrupted by hetero atoms or hetero atom groups, the synthesizing of these groups is performed preferably after forming the sulfimide group ($-SO_2-NH-SO_2-$).

First those sulfimides are prepared which contain besides the imide group at least one group having at least one easily exchangeable hydrogen atom linked to a hetero atom or a hetero atom group, which in suitable cases may also be represented by a metal atom, and hereupon these sulfimides are condensed with compounds, having

besides a lipophile group an easily exchangeable halogen atom.

According to the first step of this process organic sulfohalogenides and organic sulfamides or their metal compounds respectively or ammonia are condensed in accordance with known practice to form sulfimides. The sulfohalogenides and/or the sulfamides or their metal compounds respectively possess at least one group in the molecule with at least one easily exchangeable hydrogen atom linked to a hetero atom or a hetero atom group such as hydroxyl, mercapto, amino, sulfamino group and the like or their corresponding metal compounds respectively. If necessary instead of these groups the sulfohalogenides or sulfamides respectively may contain likewise such groups as nitro, azo, nitroso, acylamino, ester and the like groups which may be converted in the above named groups according to known practice. In this embodiment of the invention the groups having easily exchangeable hydrogen atoms are produced after the sulfimide condensation is performed.

According to the first step of the process e. g. the following sulfimides may be obtained m-hydroxy-benzene-p'-toluene-sulfimide, m,m'-dihydroxy-dibenzene-sulfimide, β -mercapto-ethane-benzene-sulfimide, p-mercapto-dibenzene-sulfimide, m - amino - benzene - p'-toluene-sulfimide, m,m'-diamino-dibenzene-sulfimide, the di-sodium salt of the methane-benzene-sulfimide-3-sulfonic acid, the 3-sulfamido-4,4'-dimethyl-dibenzene-sulfimide and the like.

As lipophile compounds having an easily exchangeable halogen atom in the molecule the following compounds may be named higher molecular halogenalkyls such as butylchloride, hexylchloride, dodecylchloride, oleylchloride and the like, halogenides of higher molecular fatty acids or naphthenic acids respectively such as butyric acid chloride, capronic acid chloride, caprylic acid chloride, caprinic acid chloride, mixtures of fatty acid chlorides or mixtures of paraffin carboxylic acid chlorides and the like, chloro carbonic acid esters of higher molecular aliphatic or cycloaliphatic hydroxyl compounds as chloro carbonic acid butyl-, -hexyl-, -octyl-, -dodecyl-, -cyclohexyl-, -methylcyclohexyl esters, halogenides of higher molecular alkyl sulfonic acids or alkyl aryl sulfonic acids as hexyl-, octyl-, dodecyl sulfochlorides or bromides, sec.-octylbenzene sulfochloride, sec.-dodecylbenzene sulfochloride, the resultant products of SO_2 and Cl_2 on aliphatic and aliphatic-aromatic hydrocarbons and the like, alkylated heterocyclic halogen compounds

The aqueous solution of this salt possesses distinguished foaming and washing properties.

Example 6

To a suspension of 33 parts by weight of 3,3'-diamino-dibenzene-sulfimide, 30 parts by weight of pyridine and 200 parts by weight of toluene while stirring at 10-20°C. drop by drop 42 parts by weight of an organic acid chloride mixture are added, which is obtained by chlorinating a fraction of carboxylic acids (b.p.₁₃=125-160° average molecular weight 158), produced by oxidizing paraffin. The mixture is stirred for some time at room temperature and is finally warmed up to

70°. After cooling down and separating the toluene by decanting, the precipitated mass is dissolved in a small amount of alcohol. To the alcoholic solution water is added and the mixture is made weakly alkaline by the addition of soda lye. The thus formed solution is evaporated in vacuo to dryness. One obtains a slight brownish powder in a nearly quantitative output, which is clearly soluble in water and which shows the same properties as the product of example 5.

WINFRID HENTRICH.

ERIK SCHIRM.

HEINZ-JOACHIM ENGELBRECHT.

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ALIEN PROPERTY CUSTODIAN

PROCESS FOR PREPARING CAPILLARY
ACTIVE SUBSTANCES

Winfried Hentrich, Rodleben B., Dessau-Rosslau,
Erik Schirm and Heinz-Joachim Engelbrecht,
Dessau, Germany; vested in the Alien Property
Custodian

No Drawing. Application filed March 26, 1941

This invention relates to capillary active substances and to a process for their preparation. More particularly it relates to a process for preparing capillary active substances from organic sulfohalogenides having at least one lipophile group in the molecule and ammonia or ammonium salts respectively in the presence of alkaline reacting agents to form sulfimides.

It is an object of this invention to provide the soap, laundry, textile, leather, fur, paper and the like industries with capillary active substances which are readily convertible into water soluble soap like salts and have excellent foaming, washing and cleaning properties.

In the co-pending application of Winfried Hentrich and Erik Schirm filed August 3, 1939, Ser. No. 288,130 there is described a process for preparing capillary active substances constituted according to the general formula



wherein at least one of the two substituents R and R' stands for an organic radical containing at least one lipophile group, which may be interrupted by hetero atoms or hetero atom groups, whereas the other radical may be any hydrocarbon radical eventually interrupted by hetero atoms or hetero atom groups, and Kat denotes any desirable cation which is capable of forming water soluble salts. The process consists in condensing sulfonic acid halogenides of the general formula $R-SO_2-Hal$ with sulfonic acid amides of the general formula $R'-SO_2-NH_2$ or its suitable metal derivatives respectively and in converting the obtained condensation products with inorganic or organic bases into water soluble salts.

In accordance with the present invention it has been found that the aforementioned process may be simplified considerably, if in the above noted formula R is equal to R'. In those cases it is not necessary to prepare the sulfonic acid amides $R-SO_2-NH_2$ separately and then to condense with the sulfonic acid halogenides $R-SO_2-Hal$, but the sulfonic acid halogenides may be reacted simply upon ammonia or any ammonium salt immediately in the presence of alkaline reacting agents, whereat two mols of sulfonic acid halogenides are applied for one mol of ammonia or the equivalent amount of an ammonium salt respectively.

Organic sulfonic acid halogenides which may be used as initial materials are e. g. 4-sec.butylbenzenesulfochloride, 4-sec.hexylbenzenesulfochloride, 4-sec.octylbenzenesulfochloride, 4-sec.dodecylbenzenesulfochloride, 4-sec.hexadecylbenzenesulfochloride, diisobutyl-naphthalenesulfochloride,

further sulfohalogenides, the hydrocarbon radicals of which are interrupted by hetero atoms such as oxygen, nitrogen or sulfur and by corresponding hetero atom groups e. g. 4-capryloyl-aminobenzenesulfochloride, 4-caprinoylamino-benzene sulfochloride, a mixture of 4-aminobenzenesulfochlorides acylated on the amino group by paraffin carboxylic acid chlorides with 7-9 carbon atoms.

According to the instant process these sulfonic acid halogenides are reacted with ammonia or ammonium salts such as ammonium acetate, formiate, carbonate, ammonium chloride and the like in the presence of alkaline reacting agents such as inorganic or organic bases or alkaline reacting salts respectively e. g. soda, soda lye, sodium acetate, calcium carbonate, pyridine and the like and if necessary in the presence of an organic solvent such as acetone, butanol, benzene, toluene or preferably in the presence of water.

Example

To a suspension consisting of 5.5 parts by weight of ammonium chloride, 100 parts by weight of water, 85 parts by weight of acetone and 60 parts by weight of 4-sec.octylbenzenesulfochloride (obtained by treating sec.octylbenzene with chlorosulfonic acid at 0-5° C) 10 n-soda lye is added drop by drop while stirring at 10-20° C in such a manner, that the mixture reacts constantly alkaline to phenolphthaleine. When the conversion begins to cease the mixture is gradually warmed up to 60° whereat the acetone distills off. The temperature of the mixture is further raised to 90° whereupon soda lye is added till the mixture finally reacts weakly alkaline. After cooling down the layer at the bottom of the liquid is dissolved in nearly 500 parts of water whereupon hydrochloric acid is added till Kongo acid reaction occurs. An oil is separated which is dissolved in ether and washed neutral with water. After drying and evaporating the ether one obtains the 4,4'-di-sec.octylbenzene-disulfimide as a highly viscous dark colored oil in an output of nearly 90% of the theory. By a treatment with soda lye the compound is converted into the corresponding sodium salt, which is soluble in water and gives strongly foaming aqueous solutions.

Instead of the 4-sec.octylbenzenesulfochloride one may use the 4-sec.dodecylbenzenesulfochloride and obtains with ammonia a condensation product the alkali salt of which is likewise water soluble and possesses a soap-like character.

WINFRID HENTRICH.

ERIK SCHIRM.

HEINZ-JOACHIM ENGELBRECHT.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE DECOMPOSITION OF CHOLESTENONE AND OF HALOGEN DE- RIVATIVES THEREOF

László Vargha and Andreas Kramli, Budapest,
Hungary; vested in the Alien Property Custo-
dian

No Drawing. Application filed March 28, 1941

The object of our invention is a process for the decomposition of cholestenone and of halogen derivatives thereof.

Our former investigations have proved, that by a quick and cautious oxidation of cholestenone in a medium of glacial acetic acid at temperatures below 15° C and by the use of only 4.5 mol of chromium oxide to 1 mol of cholestenone, after removing the unchanged starting material and the acidic by-products, practically merely progesterone can be obtained. By other known processes for the oxidation of cholestenone with chromium oxide (see e. g. Zeitschrift für physiolog. Chemie, Vol. 252, p. 49) a mixture consisting of progesterone and of androstendione has been obtained, undergoing thereafter to highly circumstantial methods of separation, connected with considerable losses of material.

Our further experiments concerning the decomposition of the cholestenone and of some derivatives thereof have proved that almost merely androstendione can be obtained by a more vigorous and lasting action of the oxidizing agent on the starting material.

We have found that cholestenone and halogen derivatives thereof advantageously can be decomposed to androstendione by oxidation of the starting material with chromium oxide in a medium of glacial acetic acid, until practically no progesterone accompanying the androstendione can be detected in the product.

Moreover we have found that the yield and the purity of the androstendione are not satisfying, if the oxidation was carried out at elevated temperatures and with great quantities of chromic oxide. Preferably the cholestenone is oxidized at temperatures below 15° C, by the action of 4.5 mol of chromium oxide to 1 mol of cholestenone during a suitable long period, lasting 24 to 48 hours. By this method satisfying quantities of pure androstendione can be separated from the products of the reaction.

By the process according to the invention one of the derivatives of the cholestenone, the 4,5,6-tribromcholestenone can be oxidized so that almost merely androstendione is obtained from the product after having removed the bromine therefrom.

Example 1

400 grammes of cholestenone are dissolved in 25 litres of glacial acetic acid and to the solution 500 grammes (4.5 mol) of chromium trioxide dissolved in 25 litres of glacial acid are added. The temperature of the reacting mixture is kept below 13 to 15° C during the addition, as well as during 48 hours following thereafter, the content of chromium trioxide of the solution being diminished thereby about to 0.4%. The unchanged chromium trioxide is then decomposed by gradual addition of methanol, taking care

thereat of keeping the temperature below 15° C. The solution is then evaporated in vacuum, below 35° C, to a volume of 20 litres and diluted with water to a volume of 80 litres. The precipitated product is twice washed with 10 litres of benzene each time, the benzene-extract is washed with water, with 2 n-sodium hydroxyde and then with water again, dried with anhydrous sodium sulphate and evaporated in vacuum. The volatile components of the residue are separated by steam-distillation and the remaining product is dissolved in 1.5 litres of benzine. The benzine-solution is shaken out two times with 500 cubic centimetres of 2 n-sodium hydroxide each, and then with distilled water. In order to separate the androstendione the benzine-solution is extracted three times with 1500 cubic centimetres of concentrated hydrochloric acid and the united acid-solutions are diluted to a volume of 12 litres. The androstendione precipitated in a fine emulgated condition is twice shaken out with 2 litres of ether, the ether-solution is washed with water, with n-sodium hydroxide, with diluted hydrochloric acid and with water again, dried with anhydrous sodium sulphate and then evaporated to dryness, 7.2 grammes of a light-yellow coloured oil are obtained, from which after adding some ether and cooling 2.5 grammes of pure androstendione crystallize out. From the mother liquor further quantities of androstendione can be obtained. The product re-crystallized from ether shows a melting point of 167–170° C. From the benzine-solutions remaining after the treatment with hydrochloric acid 100 grammes of cholestenone can be recovered.

Example 2

62.4 grammes of pulverized crude 4,5,6-tribromcholestenone are suspended in 2500 cubic centimetres of glacial acetic acid and to the stirred solution 75 g (7.5 mol) chromium trioxide dissolved in 40 cubic centimetres of water and 400 cubic centimetres of glacial acetic acid are added during a period lasting 4 hours. During the addition the temperature of the reacting mixture is kept at 35° C and thereafter, during 24 hours, at 15° C.—50 cubic centimetres of methanol are then added to the cooled solution and, after the decomposition of the abundance of chromium trioxide the bromine is removed by adding 100 grammes of zinc powder, keeping the temperature below 35° C thereat. The filtered solution is evaporated at 35° C to a volume of 700 cubic centimetres and the residue is worked up according to the method disclosed in Example 1. The end-product is 1 gramme of a glass-like material containing 280 milligrammes of androstendione. 12 grammes of cholestenone are obtained as a by-product.

LÁSZLÓ VARGHA.
ANDREAS KRAMLI.

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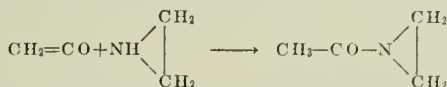
N,N-(ALPHA - BETA - ALKYLENE) - ACETAMIDES AND A PROCESS OF PREPARING THEM

Herbert Bestian, Frankfurt am Main-Hoechst, Germany; vested in the Alien Property Custodian

No Drawing. Application filed March 28, 1941

The present invention relates to N,N-(alpha-beta-alkylene)-acetamides and to a process of preparing them.

I have found that N,N-(alpha-beta-alkylene)-amides of acetic acid are obtained by the reaction of ketene and alpha-beta-alkylene-imines. The reaction which consists in an addition of alpha-beta-alkylene-imine to ketene occurs, for instance as regards ethylene-imine, according to the following structural formula:



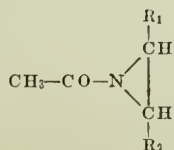
It may be advantageous to carry through the reaction in a solvent or diluent and to take care, by an effective cooling of the reaction vessel, that the heat being set free in a considerable portion during the addition process is led off. The solvents or diluents have suitably to be indifferent to ketene and the alpha-beta-alkylene-imine; there may be used, for instance, aliphatic ethers, hydrocarbons such as benzene, toluene, xylene, benzine, cyclohexane furthermore halogenated hydrocarbons such as carbon tetrachloride or chlorobenzene. Water, however, is likewise suitable as a reaction medium.

Since 1 mol of the ketene reacts with 1 mol of the alkylene-imine, the starting materials are suitably used in about equimolecular proportions.

The reaction occurs already at very low temperatures. It is advantageous to choose not too high a temperature since otherwise the final products would polymerize. The reaction may, however, still be carried through at a temperature of about +60° C.

The N,N-alkylene-amides of the acetic acid obtained by the process in a good yield are best purified by distillation under reduced pressure. On working up the products obtained the presence of compounds of an acid action has to be avoided since in the acid pH-sphere a transformation of the products into polymers readily occurs.

As starting materials there may for instance be used alpha-beta-ethylene-imine, alpha-beta-propylene-imine, 1,2-butylene-imine, 2,3-butylene-imine and corresponding imines of higher aliphatic hydrocarbons as well as of aromatic hydrocarbons, for instance dodecyl-alpha-beta-ethylene-imine and phenyl-alpha-beta-ethylene-imine. There are obtained compounds of the general formula:



wherein R₁ and R₂ stand for hydrogen or a hydrocarbon radical.

The compounds obtained may be used as intermediate products for the manufacture of plastics and adjuvants in the textile industry.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight:

(1.) A three-necked apparatus, provided with a stirrer, a dropping funnel and a thermometer is used for the reaction. The reaction vessel is cooled with carbonic acid ice and acetone.

750 parts of anhydrous ether are first introduced into the apparatus and 210 parts of ketene are then added; the ketene dissolves in the strongly cooled ether. To the solution thus obtained a solution of 215 parts of ethylene-imine in 250 parts of anhydrous ether is caused to flow in the course of 1-2 hours. The reaction occurs with a considerable heat effect. After the entire portion of ethylene-imine has been caused to flow in, the cooling device of the reaction vessel is removed and the temperature is allowed to rise to room temperature. The solution is worked up by distillation. After the distillation of the ether is complete there is obtained the N,N-ethylene-acetamide in the form of a dark red liquid boiling between 42° C and 45° C under a pressure of 15 to 20 mm of mercury.

The N,N-ethylene-acetamide obtained in a good yield according to the afore-described process constitutes a transparent, readily mobile liquid of an odor resembling pyridine and piperidine. The liquid is readily soluble in water and all the usual organic solvents. In the pure condition it is stable without decomposition, whereas in the presence of acid acting compounds, for instance sulfurous acid, it may be polymerized so as to obtain a highly viscous compound.

(2.) A solution of 210 parts of ketene in 750 parts of ether is prepared as described in Example 1 in the apparatus named in the preceding example. A mixture of 285 parts of alpha-beta-propylene-imine in 250 parts of anhydrous ether is caused to flow to the solution in the course of 1 to 2 hours. The reaction occurs with a considerable effect of heat. After the addition of the propylene-imine is complete, the cooling device of the reaction vessel is removed and the temperature is allowed to rise to room temperature. The solution is worked up by distillation. The N,N-(alpha-beta-propylene)-acetamide which distills between 52° C and 55° C under a pressure of 15 to 20 mm of mercury is obtained in a good yield in the form of a transparent liquid. The compound has the same properties as the N,N-ethylene-acetamide described in example 1.

(3.) 25 parts of ketene are introduced without cooling the apparatus from outside, while stirring, into a solution of 21.5 parts of ethylene-imine in 300 parts of ether. The temperature

rapidly increases to 35° C so that the ether boils in a reflux condenser. After half an hour the introduction of the ketene is complete. The ether is evaporated and the N,N-ethylene-acetamide formed is distilled under reduced pressure. The yield amounts to 37 parts, i. e. 87 per cent of the theoretical yield.

(4.) 50 parts of ketene are introduced in the course of 1 to 2 hours, while stirring and cooling with water of 15° C to 20° C, into 43 parts of

ethylene-imine of 100 per cent strength. During this operation the temperature increases to 40°-45° C. As soon as the effect of heat has ceased, the reaction of the ethylene-imine is complete. By a distillation under reduced pressure there is obtained the pure N,N-ethylene-acetamide in a yield of 79 parts, i. e. 93 per cent of the theoretical yield.

HERBERT BESTIAN.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREPARATION OF DYE-STUFFS OF THE ANTHRACENIC SERIES

Robert Henri Léon Bretagne, Nogent-S/Oise, France; vested in the Alien Property Custodian

No Drawing. Application filed April 3, 1941

It is known that the condensation of 9.10 disulphuric esters of leuco-anthraquinones containing an amino group acylated or not, in the beta position, or of the salts of the said esters, can be carried out in an alkaline medium by means of various oxidizing products or salts which have the property of acting as such when passing at the lower valency. The products of the condensation are esters of the N-dihydro-1.2.2'.1' anthraquinone.azine or of its substituted derivatives, which have a great value from the tinctorial point of view, especially in printing.

All oxidizing products up to now proposed have more or less evident disadvantages. Some have an action that is not limited to condensation only, others produce salts which are partially soluble in an alkaline medium, when they have given off one atom of oxygen. These salts contaminate the dyestuff, which necessitates an ulterior purification.

The present invention has for its object the use of silver oxide as agent for the condensation of the leuco-esters of the 2-amino-anthraquinone and of its substituted products (position 1 remaining free). The oxidizing products used previously, were known condensation agents, such as potassium permanganate, ferric chloride, sodium hypochlorite, potassium ferricyanide, potassium persulphate or lead peroxide. On the contrary, silver oxide has never been used up to now as a condensation agent. Now, according to the invention, it has been found that silver oxide permits not only to condense two molecules of di-ester with a sufficient yield, but also to completely recover the silver, the product of the decomposition of the oxide being completely insoluble in alkaline medium, after reaction.

The oxygen evolved during the reaction does not act upon the organic molecule, but combines itself with the two atoms of hydrogen freed by that one, to form water. The beta-amino anthraquinone sulphuric di-ester, or its substituted derivatives, are soft reducing agents of the silver oxide and metallic silver at a granulated state is obtained at the end of the reaction. A silver mirror is not formed at any moment, the grey powder adheres slightly to the walls of the vessel in which the condensation takes place and even gets loose at the end of the reaction.

The condensation can be accomplished either with dry silver oxide, or recently prepared and as a paste, either with its ammoniacal solution, or also with silver oxide formed directly in the mixture which will enter into reaction. In this case, it is possible to start indifferently from solu-

ble or not soluble silver salts, able to give oxide in an alkaline medium.

The totality of the silver can be recovered after the reaction, and can easily be transformed into a soluble salt, which permits an easy regeneration of the oxide and the elimination of small proportions of organic products.

The following are non limiting examples for the application of the invention.

Example 1

500 parts of water, 20 parts of sodium carbonate and 18 parts of beta-amino-anthraquinone sulphuric di-ester are heated at a temperature of 100°C, and 14 parts of silver oxide are then charged in small equal portions. The temperature is maintained till the end of the transformation, the mixture is cooled, filtered and the silver precipitate is washed. The dyestuff, as tetra-ester, is in solution in the filtrate. It is isolated in the usual manner.

Example 2

450 parts of water, 50 parts of caustic soda of 30% and 18 parts of 2.amino.3.chlor.-anthraquinone sulphuric di-ester, are heated at a temperature above 80°C and 10 parts of silver oxide are gradually charged (as a paste). The temperature of the mixture is maintained a few minutes and the process is then carried out as in Example 1.

Example 3

A solution of 30% of silver nitrate (65 parts) is slowly and regularly poured in a hot solution composed of 450 parts of water, 65 parts of caustic soda of 30% and 18 parts of 2.amino.3.chlor.-anthraquinone sulphuric di-ester. The temperature of the mixture is maintained till the end of the reaction. The mixture is filtered after cooling and the dyestuff is isolated in the usual manner.

The silver precipitate is then treated by diluted nitric acid, in the hot. The solution, filtered in order to eliminate the organic products, can be concentrated in order to recover the salt in a solid state or neutralized and used directly for a new condensation.

Example 4

14 parts of silver chloride, as a paste, are charged gradually in small equal portions, in 400 parts of water, 40 parts of caustic soda of 30% and 14 parts of 2.amino.3.chlor.-anthraquinone

sulphuric di-ester, heated above 80°C. The temperature is maintained a few minutes and the dyestuff, after cooling and elimination of the silver, is isolated.

Example 5

480 parts of water, 60 parts of caustic soda of 30%, 7 parts of 2.amino.3.chlor.-anthraquinone sulphuric di-ester, are heated under pressure at 120°C during 15 minutes. After elimination of the silver, and precipitation by a mineral acid, the dyestuff gives a blue shade in the vat dyeing.

Example 6

In a solution, maintained at a temperature above 80°C, which contains 400 parts of water, 32 parts of caustic soda of 30% and 7 parts of 2.amino.3.chlor.anthraquinone sulphuric di-ester, is poured a solution prepared with 100 parts of water, 17 parts of caustic soda of 30%, 10 parts of silver nitrate and 20 parts of ammonia of 25%. The isolation of the dyestuff is carried out as in the preceding examples.

ROBERT HENRI LÉON BRETAGNE.

ALIEN PROPERTY CUSTODIAN

ADHESIVES AND A PROCESS OF PRODUCING SAME

Theodor Daur, Mannheim, and Walter Daniel,
Ludwigshafen-on-Rhine, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed April 4, 1941

The present invention relates to new adhesives and a process of producing same.

Solutions of film-forming adhesive substances, for example of natural or synthetic resin, rubber or polyvinyl compounds in a monomeric polymerizable substance, for example in monovinyl compounds, such as monomeric styrene, vinyl esters, acrylic or methacrylic esters, chlorobutadiene or dimethylbutadiene, are known to be suitable as adhesives for joining materials. The said solutions are applied to the surfaces to be cemented together, the surfaces are contacted and the monomeric compounds are polymerized. The polymerization of the monomeric compound may be accelerated by heating and/or by adding a known polymerization catalyst, especially peroxides, for example benzoylperoxide, or persulphates. A strong and lasting joint between the cemented parts is thus obtained; since it is not necessary to remove volatile constituents (as is the case if adhesives dissolved in volatile non-polymerizing solvents are used), no formation of blisters and voids in the cementing layer occurs.

Solutions of film-forming adhesive substances in polymerizable solvents possess, however, but a limited storage capacity in view of the tendency of such solvents to polymerize. Frequently partial polymerization of the monomeric solvent takes place already after about 2 to 3 weeks or, depending on the temperature, after a longer time, causing the adhesive solution to solidify to such a degree as to make it unsuitable for being spread. Since the adhesive solution, on the other hand, is required to solidify comparatively quickly in use, solvents which are easily polymerized must necessarily be employed, so that the lack of sufficient storage capacity cannot be overcome by resorting to substances which are somewhat more difficult to polymerize.

The polymerization of vinyl compounds, as is known, may be prevented or highly retarded by the addition of stabilizing media, for example compounds containing nitrogen, oxygen or sulphur, such as aniline, pyrogallol, hydroquinone and mercaptans. These stabilizing media, however, must be removed again when the vinyl compounds so stabilized are to be polymerized. Since practically all of the known stabilizing media are high-boiling substances, the stabilizer either must be washed out, for example with acid or lye, or the vinyl compound must be distilled. Such measures, however, are not applicable to adhesive solutions or are much too troublesome.

We have now found that adhesive solutions comprising organic adhesive substances in liquid

polymerizable compounds can be excellently stabilized by adding thereto small amounts of readily volatile compounds containing nitrogen, oxygen or sulphur, as stabilizing agents. These substances prevent the adhesive solutions from undesired premature solidification, but evaporate very quickly when the adhesive solutions are applied and leave the polymerizable compound in a readily polymerizable state. The evaporation of the stabilizing agent may be promoted by gentle heating, if desired, the polymerization of the polymerizable compounds being simultaneously accelerated. In many cases, however, the stabilizers evaporate already completely when the adhesive solutions are applied, so that no additional measures are needed.

Suitable readily volatile stabilizing media are compounds containing nitrogen, oxygen or sulphur boiling below about 40°C, such as for example, acetaldehyde, ethylamine, ammonia, hydrogen sulphide, methyl and ethyl mercaptan. The said stabilizing agents are added in small amounts. Additions of less than 0.1 per cent are often sufficient to render the adhesive solutions sufficiently stable. The adhesive solutions should, of course, be kept and stored in well-closed receptacles, lest the stabilizing media should escape prematurely. In special cases higher percentages of the stabilizing media than 0.1 per cent may also be employed, for example 0.5 or 1 per cent or up to 5 per cent.

It is preferable to add in known manner polymerization accelerators to the adhesive solutions prior to the use, for example about 2 per cent of benzoylperoxide. Excellent joints are obtained by means of the new adhesives in a short time.

The following Example serves to illustrate how the present invention may be carried out in practice but the invention is not restricted to this Example. The parts are by weight.

Example

10 parts by weight of a rubber conversion product (obtained by the action of phosphorus oxychloride on natural rubber) are dissolved in 90 parts by weight of monomeric styrene. Portions of the adhesive solution thus obtained are stabilized each with one of the highly volatile stabilizing media listed below, and allowed to stand for 50 hours at 20° C in closed vessels. 5 grams of each solution was then diluted with 100 cubic centimeters of carbon tetrachloride and the diluted solutions were tested in the Ubbelohde viscosimeter. By way of comparison two samples of the same solution of rubber conversion product

in monomeric styrene without a stabilizer were tested in the same manner (diluted with carbon tetrachloride), one sample directly after its preparation and the other after 50 hours' standing at 20° C in a closed vessel. The solution without stabilizer after standing has polymerized to such an extent as to be no longer soft enough for being spread. The data for the fluidity of all the solutions tested in the Ubbelohde viscosimeter can be seen from the following table:

Solution	Stabilizer	Quantity of stabilizer	Time of flow
Fresh	None		Seconds
After 50 h. at 20° C	do		133.8
Do.	Acetaldehyde	2 drops per 100 grams of adhesive solution.	316.6
Do.	Conc. aqueous ammonia	do	242.0
Do.	Ethylamine	do	161.0
Do.			162.7

The solution added with one of the afore-mentioned stabilizers and admixed with 2 per cent of benzoyl peroxide was applied to a sheet of highly polymerized isobutylene in which a filler has been incorporated. The sheet is then placed on a sheet iron plate, which has likewise been brushed with the adhesive solution, and slightly pressed on. After 2 days the parts so cemented together have become so strongly joined that it would

mean destruction to the sheet to detach it from its support. An unstabilized adhesive solution of otherwise the same composition takes the same time to harden.

5 Equally good results are obtained with solutions of 30 parts of chloro-rubber in 70 parts of monomeric styrene or of 20 parts of colophony in 80 parts of monomeric styrene or of 30 parts of polymeric isobutylene (molecular weight about 10 30,000) in 70 parts of monomeric styrene, while adding about 0.1 per cent of monoethylamine as a stabilizer. It is advantageous to add to the solution before use about 2 per cent of benzoyl peroxide; then the solution yields very strong and lasting joints within 2 days at ordinary temperature. Sheets or films from artificial masses, paper, tissue, wood, metals and stone may thus be well joined to one another.

15 Instead of styrene, β -chlorbutadiene or 1,4-dimethylbutadiene may also be employed.

20 An excellent adhesive which may well be stored is obtained by preparing a solution of 40 parts of an interpolymerization product of vinyl chloride and vinyl ethyl ether in 60 parts of methacrylic acid methyl ester, to which about 0.1 per cent of methylamine is added as a stabilizing agent. 1 per cent of benzoyl peroxide is preferably added to the solution before use.

30 THEODOR DAUR.
WALTER DANIEL.

ALIEN PROPERTY CUSTODIAN

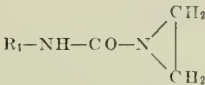
PROCESS OF STICKING OR CEMENTING AND
STICKING OR CEMENTING AGENTS

Herbert Bestian, Frankfurt am Main, and Eugen
Bock, Krefeld-Uerdingen, Germany; vested in
the Alien Property Custodian

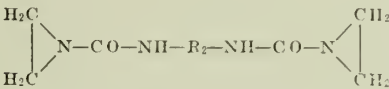
No Drawing. Application filed April 5, 1941

The present invention relates to a process of
sticking or cementing and to sticking or cement-
ing agents.

We have found that particularly stable stick-
ings or cementations between the most various
substances may be obtained by applying between
the substances to be cemented and, thereupon,
completely polymerizing compounds of the
general formulae:



and



wherein R₁ stands for hydrogen or a univalent
aliphatic or isocyclic radical and R₂ for a divalent
aliphatic or isocyclic radical or the homologues
or derivatives thereof or the products obtained by
partial polymerization of these compounds. The
compounds corresponding to the above formulae
may be obtained by condensation of isocyanates
with 1,2-alkylene-imines. There may be used,
for instance, the monomeric compounds and the
partially polymerized products thereof which are
described in the co-pending applications Serial
No. 322,031 and Serial No. 322,032 both filed
March 2, 1940, in the name of Herbert Bestian,
for "Polymerization products."

The mode of application of the sticking or
cementing agents depends upon the nature of the
materials to be cemented. They may serve for
the production of cementations in the monomeric
state in case the surfaces of both substances to
be cemented are not porous, for instance, two
metal surfaces. Otherwise, there are advan-
tageously used products obtained by partial poly-
merization which, owing to their high viscosity
even in the heat, are not absorbed by the porous
substances. For producing stickings or cemen-
tations by means of such products as are obtained
by partial polymerization there are suitable those
prepared in the fused state as well as those pre-
pared with application of a solvent, such as, for
instance, water or butanol. Also mixtures of two
or more compounds of the above general formulae
may be used in the monomeric or polymerized
state. Furthermore, it is possible to add to the
compounds softening agents, for instance, phthal-
ic acid dibutylester, tributylphosphate, triphenyl-
phosphate, octyl alcohol as well as extenders and
known sticking or cementing agents such as wood
dust, kaolin, diatomaceous earth, natural and
artificial resins, cellulose derivatives, casein, al-
bumin, gluten, vegetable flours such as potato
starch, especially when made up into a paste, or

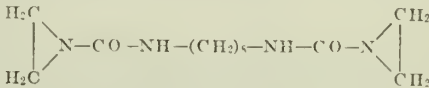
the like. By addition of formaldehyde a substan-
tial acceleration of the setting process is attained.

Two solid materials are preferably cemented by
applying the cementing substance in the mono-
meric or partially resinified state onto the sur-
faces to be united and by, thereupon, completely
polymerizing the said substance by applying pres-
sure and heat. The polymerization may be
effected according to the conditions described in
the two co-pending patent applications mentioned
above.

The above ureas or their polymerization prod-
ucts are suitable for cementing wood, metal, glass,
plastics, paper, fabric or the like as well as for
uniting substances of different kind, for instance
for uniting metal and glass, plastics and glass,
wood and metal and so on.

The following examples serve to illustrate the
invention but they are not intended to limit it
thereto, the parts being by weight:

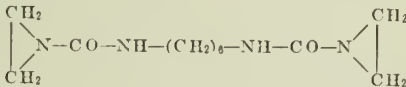
(1) Two aluminium sheets of 2 mm thickness
are well cleaned on the surfaces to be united. On
both these surfaces a thin layer of a butanol solu-
tion of 50 per cent strength of the partially poly-
merized urea of the formula:



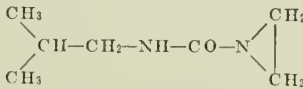
is applied. Thereupon, the said two surfaces are
placed one upon the other, pressed together by
weight and thereafter dried for 3 hours in a dry-
ing oven at 120° C. A very stable cementation is
obtained and the two surfaces are inseparable
even at high temperatures.

The monomeric urea of the above formula is
obtained by reaction of 1,8-octamethylene-di-
isocyanate with ethylene in acetone solution. The
butanol solution of 50 per cent strength used for
the cementation is prepared by heating for 2-3
hours at 80° C to 90° C equal parts of the mono-
meric urea of the above constitution and of
butanol.

(2) 80 parts of the urea of the following
formula:



and 20 parts of the urea of the following formula:



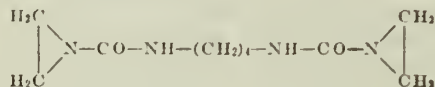
are heated for a short time at 110° C until a clear
melt has been formed. The temperature of the
molten mass is then reduced to 80° C and this
temperature is maintained until the resinification
of the urea mentioned in the first place has pro-

ceeded so that, on cooling, it does not tend to crystallize. The subsequent heating takes about 1-2 hours. A viscous mass is obtained which is perfectly suitable for preparing cementations.

A glass rod of quadratic cross section is coated on one of its longitudinal surfaces with the cementing mass thus obtained, slightly pressed onto a glass plate and then heated in a drying oven for 2 hours at 120° C. A glass-clear cementation of the two glass pieces is obtained which even by application of heat cannot be dis- united. By employing force, the glass breaks but the cementation does not give way.

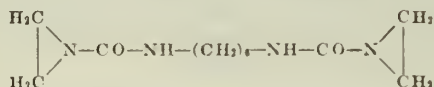
Both ureas of the above formulae are obtained by reaction of 1,6-hexamethylenediisocyanate and isobutylisocyanate, respectively, with ethylene-imine.

(3) The urea obtained by reaction of 1,4-tetra- methylene-diisocyanate with ethylene-imine and corresponding to the following formula:



is strewn in the form of a powder on an alumin- ium sheet. A glass sheet is placed thereon, the two sheets are pressed together by a small weight and thereupon heated for 2 hours in a drying oven at 110° C to 120° C. The glass adheres very firmly to the aluminium and cannot be detached even at raised temperature.

(4) A plywood plate of beech is prepared by coating a beech veneer of 2 mm thickness on both sides with an aqueous solution of 50 per cent strength of a partially polymerized product of the formula:



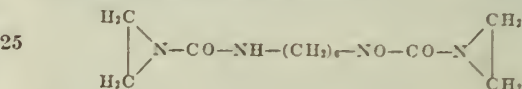
placing on both sides each a veneer not coated with the glueing agent in such a manner that the grains of the veneers are at right angles to the inner veneer coated with the glueing agent, plac- ing the whole in a hydraulic press with plates having a temperature of 120° C and maintaining it under pressure for 30 minutes. Thereafter, the individual veneers cannot be separated from

each other. By violently tearing the plywood, the wood cracks but the cementations are not separated. They are also entirely stable against cold and hot water.

5 The partially polymerized product is obtained by stirring 1 part of the monomeric product ac- cording to the above formula with 1 part of water and heating to 90° C to 100° C. After heating for about 13 minutes the polymerization is 10 stopped by cooling. The viscous solution is used for glueing.

In case the solution of the partially polymer- ized product is not directly used, it may be ren- dered stable by addition of ammonia. Instead 15 of applying the liquid solution of the sticking agent to the part to be glued, a fabric or paper may be impregnated therewith and the film thus prepared may be used for cementing.

(5) 78 parts of water are poured on 20 parts 20 of casein (lactic-acid casein) and, after swelling, the casein is dissolved by addition of 2 parts of ammonia of 25 per cent strength. Thereupon, 10 parts of urea of the formula:



are added.

A plywood is prepared from 3 veneers of beech 30 wood of 2 mm thickness by coating both sides of the middle veneer with the solution of the stick- ing agent, whereas the outside veneers are ap- plied in the uncoated state. The joinery board is pressed for 10 minutes in a hydraulic press 35 heated to 100° C. When test bodies are broken in order to ascertain the shearing strength ac- cording the prescriptions of the "Reichsaus- schuss für Lieferungsbedingungen" a resistance of the cementation of 34 kg/cm² is obtained.

40 (6) Instead of 10 parts of the monomeric urea of example 5 there are used 10 parts of the aque- ous, partially polymerized urea of 50 per cent strength prepared according to example 4. By 45 proceeding according to example 5, the same re- sistance to shearing as according to this example is obtained.

HERBERT BESTIAN.
EUGEN BOCK.

ALIEN PROPERTY CUSTODIAN

ESTERS OF ALCOHOLS OF THE ACETYLENE SERIES

Otto Schlichting and Karl Klager, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 5, 1941

The present invention relates to esters of alcohols of the acetylene series, more particularly to carboxylic and sulfonic acid esters of propinol-3 ($\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$) and butinol-3



It is known that compounds of the acetylene series are distinguished from other aliphatic compounds in that the hydrogen atoms attached to the $-\text{C}\equiv\text{C}-$ group are particularly reactive. These hydrogen atoms may be replaced by metal or organic radicles. Phenylacetylene, for example, may be converted into ketones by causing the sodium compound of phenyl acetylene to react with carboxylic acid chlorides. Even alcohols of the acetylene series differ from other aliphatic alcohols. When oxidizing, for example, propinol-3 in the form of its copper compound, there is obtained hexadiene-diol whereas the hydroxy group remains unchanged. Due to the difference of alcohols of the acetylene series from other aliphatic alcohols, carboxylic and sulfonic acid esters of such alcohols have hitherto not been prepared.

We have now found that carboxylic and sulfonic acid esters of propinol-3 and butinol-3 may be prepared in a simple manner by causing carboxylic acid anhydrides or halides or sulfonic acid halides to act on propinol-3 or butinol-3 in the liquid phase in the presence of water.

Suitable anhydrides and halides are for example those of mono- and polybasic aliphatic carboxylic acids, e. g. of acetic acid, propionic acid, succinic acid, maleic acid or adipic acid, of araliphatic or aromatic mono or polycarboxylic acids, e. g. benzoic acid, nitrobenzoic acid, chlorobenzoic acid or phthalic acid, or of heterocyclic carboxylic acids, e. g. pyridine carboxylic acid. Suitable sulfonic acid halides are for example propane sulfonic acid chlorides and the sulfonic acid chlorides obtainable by the reaction between saturated aliphatic or cycloaliphatic hydrocarbons and sulfur dioxide and chlorine as well as benzene or para-toluene sulfonic acid chloride.

In order to effect the esterification, the propinol-3 or butinol-3 which may be dissolved in water, is admixed at normal temperature or while cooling with the acid anhydride or halide. An agent capable of binding acids, for example the calculated amount or an excess of an alkali metal hydroxide, carbonate, an alkali earth metal hydroxide or carbonate or tertiary amino compounds, is then added, while simultaneously stirring the reaction mixture. The esters formed

are insoluble in water and may be easily separated from the aqueous reaction mixture. They may be purified by distillation.

As already mentioned, the reaction may be carried out at normal temperature or at lower temperature. It is, however, possible to work at elevated temperature, for example while boiling the reaction mixture under reflux cooling.

The esters of propinol-3 and butinol-3 obtained according to the present invention are suitable for introducing directly acetylene radicles into organic compounds.

The following examples will further illustrate how the present invention may be carried out in practice. However, the invention is not restricted to these examples.

Example 1

1500 grams of benzene sulfonic acid chloride are admixed at 0°C with 4200 grams of a 25 per cent aqueous solution of propinol-3. 100 cubic centimeters of a 35 per cent sodium hydroxide solution are allowed to flow slowly into this mixture, while stirring and cooling to 0°C . After having stirred for several hours, the solution has become neutral. The benzene sulfonic acid ester of propinol-3 separates in the form of an oil. The yield amounts to from 90 to 95 per cent. The ester may be purified by distillation under reduced pressure. It boils at $142-144^\circ\text{C}$ under 4 millimeters pressure.

From 76.2 grams of para-toluene sulfonic acid chloride, 250 grams of a 25 per cent aqueous solution of propinol-3 and 50 cubic centimeters of a 35 per cent aqueous solution of sodium hydroxide there is obtained under otherwise identical conditions the para-toluene sulfonic acid ester of propinol-3. It boils at $161-162^\circ\text{C}$ under 4 millimeters pressure.

Example 2

600 grams of a 25 per cent aqueous solution of propinol-3 are cooled to 20°C below zero and admixed with 140 grams of benzoic acid chloride. 114 cubic centimeters of an aqueous 35 per cent solution of sodium hydroxide are allowed to flow slowly into this emulsion while stirring at 20°C below zero. The reaction mixture is then allowed to warm up slowly to room temperature. It then has a neutral reaction. The benzoic acid ester of propinol-3 formed is extracted with ether, the ethereal solution washed with water, the ether removed and the ester distilled under reduced pressure. It boils at $103-109^\circ\text{C}$ under 8 millimeters pressure. The yield amounts to 85 per cent.

When starting from 600 cubic centimeters of a 25 per cent aqueous solution of propinol-3, 102 grams of acetic acid anhydride and 114 cubic centimeters of an aqueous 35 per cent solution of sodium hydroxide, there is obtained the acetic acid ester of propinol-3, boiling at 111–112°C.

Example 3

23 grams of a 35 per cent aqueous solution of sodium hydroxide are allowed to flow slowly into a mixture of 23.2 grams of a 60 per cent solution of butinol-3 and 35.3 grams of benzene sulfonic acid chloride, while stirring at 0° C. After having stirred for several hours, the mixture has become neutral. Two layers are formed. The oily layer is separated from the aqueous layer. The benzene-sulfonic acid ester of butinol-3 is thus obtained in a yield of 80 per cent.

Example 4

170 grams of an aqueous 35 per cent solution of sodium hydroxide are allowed to flow slowly into a mixture of 116.6 grams of a 60 per cent aqueous solution of butinol-3 and 285.2 grams of para-toluene sulfonic acid chloride, while stirring at 30–40° C. Stirring is continued until the reaction mixture has become neutral. The solution is then cooled with ice and diluted with 300 cubic centimeters of water. The para-toluene sulfonic acid ester of butinol-3 separates in the form of crystals which are filtered off and washed with water. The yield is 87 per cent. After recrystallization from cyclohexane, the ester melts at 58–60° C.

Example 5

86 grams of an aqueous 35 per cent solution of sodium hydroxide are allowed to flow drop by drop into a suspension of 58.3 grams of butinol-3 (in 60 per cent aqueous solution) and 76.5 grams of acetic acid anhydride which suspension

has been cooled to 20° C below zero. The mixture is then allowed to warm up slowly to room temperature, while stirring until it has become neutral. After having added 100 cubic centimeters of water, the ester formed is separated off as an oil, dried with anhydrous sodium sulfate and distilled. It boils at 124–126° C. The yield is 45.6 grams corresponding to 81.5 per cent.

Example 6

172 grams of an aqueous 35 per cent solution of sodium hydroxide is allowed to flow drop by drop into a mixture of 116.7 grams of butinol-3 (in 60 per cent aqueous solution) and 210 grams of benzoic acid chloride which mixture has been cooled to 10° C below zero. The whole is then stirred at room temperature until the reaction has become neutral. After having added 200 cubic centimeters of water, the whole is cooled down to 0° C, the ester formed is filtered off and washed with water. After recrystallization from ligroin this benzoic acid ester of butinol-3 melts at 27–30° C. The yield is 155 grams corresponding to 88.7 per cent.

Example 7

114 cubic centimeters of an aqueous 35 per cent sodium hydroxide solutions are allowed to flow drop by drop into a mixture of 600 cubic centimeters of an aqueous 23.6 per cent solution of propinol-3 with 185.5 grams of para-nitrobenzoic acid chloride while stirring at 10–20° C below zero. Cooling is then discontinued and the mixture stirred at room temperature until it has become neutral. The precipitate formed is filtered off, washed with dilute sodium carbonate solution and dried. 150 grams of para-nitrobenzoic acid ester of propinol-3 are thus obtained. After recrystallization from ligroin it melts at 89–90° C

OTTO SCHLICHTING.
KARL KLAGER.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF SYNTHETIC TANNING MATERIAL

J. Seidel, Oybin, near Zittau, and Helmut Weber,
Grottau, Sudetenland, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed April 8, 1941

This invention relates to a method for the production of synthetic tanning material and to the products of said method.

It is known to use the waste lye of sulphite cellulose which is a by-product in the production of cellulose, as an initial material for the production of tanning material.

We have now found that tanning materials of very desirable properties can be obtained by adding to the waste lye such a quantity of acid as is required for converting the ligninesulphonic calcium contained in the waste lye, and condensing the waste lye together with organic compounds containing certain atoms or atom groups which have a close affinity to the protein of the skin, using aldehydes or ketones as condensing agents.

Advantageously an organic or inorganic acid is added to the waste lye which furnishes soluble calcium compounds, such as, formic acid, lactic acid, glycol acid, hydrochloric acid. This offers the advantage that the condensation is accelerated and leather of lighter colour can be obtained.

Suitable atoms or atom groups adapted to produce tanning material together with the lignine matter of the waste lye, are stated hereunder, viz:

1. —OH groups in aromatic and aliphatic compounds,
2. —SH groups in aromatic and aliphatic compounds,
3. =O groups in aromatic compounds,
4. —NH₂ groups in aromatic and aliphatic compounds,
5. =CO groups in aromatic and aliphatic compounds.

Representative of substances containing such atom groups are: Mono- and polyvalent phenols, cresols, and their derivatives, naphthols, oxypyridines, thiophenols, thionaphthols, chinons, urea and thiourea, as well as derivatives of said groups.

Moreover, it has been found that carbohydrides, for instance, starch and the decomposition products thereof, such as, swelling starch, soluble starch and dextrine or mixtures of these decomposition products in connection with the above mentioned substances containing the specified atom groups are excellent constituents.

According to a known method solutions containing ligninesulphonic acid with aromatic hydroxy-compounds are condensed by means of aldehydes in a strongly acid agent. The condensate, which is separated from the reaction mixture in a solid form, cannot be used as a tanning

material in this form, but has to be freed from the acid and adjusted to a suitable pH-value.

According to the present invention, on the other hand, the waste lye is condensed after the required amount of acid has been added. After the condensation no further treatment such as acidification or alkalisation is required, but the condensate can be drawn off and used as a tanning material in the form in which it is obtained in the reaction mixture. The condensate are liquid products which are readily soluble in cold water.

A wide range of different effects can be produced regarding the resulting leather by the use of several condensable constituents of the above specified types which may be added successively in a suitable temporal order. Any kind of leather ranging from stiff sole leather to the thinnest upper leather can be made by means of the tanning materials produced after our novel process.

The tanning materials produced in this manner can be mixed with any natural and with any known synthetic tanning materials in any desired proportion. Moreover, they may be used with admixtures of inorganic salts, for example, chromium, zinc or aluminum salts.

Furthermore, we have found that a noticeable lightening of the leather can be achieved by adding to the condensate neutral or slightly acid salts of organic sulpho-acids, for instance, sulphophenate of sodium or phenol-sulphonic sodium, cresol-sulphonic sodium, or benzol-sulphonic sodium.

It will thus be understood that the waste lye is not condensed with a condensable compound in the presence of a free organic sulpho-acid, by means of aldehyde or ketones. In the known reaction of waste lye with organic sulpho-acids, whose condensates have to be acidulated, dark coloured products are obtained. The dark colour is attributed to an oxidation of the sugar and other substances contained in the waste lye and tending to resinification. This property of substances containing products formed by reaction of waste lye with organic sulpho-acids has an undesirable effect upon the colour of the leather which is avoided according to the present invention.

Example 1

100 parts of waste lye are heated with 5 parts of formic acid to a temperature of 50 to 60° C, for a period of 30 minutes; 10 parts of resorcin and 10 parts of formaldehyde are admixed and the mixture is treated by means of a reflux cooler at

80° to 90° C for a period of 3 hours. The resulting tanning material is fully soluble in water and produces a soft, full leather.

Example 2

100 parts of waste lye are heated with 5 parts of lactic acid to a temperature of 50° to 60° C for a period of 30 minutes; 10 parts of resorcin are admixed with continuous stirring. After thorough mixing 15 parts of dextrine and 10 parts of formaldehyde are admixed, and the mixture is treated at 80° to 90° C at a reflux cooler for 4 to 5 hours. The resulting tanning material is water-soluble and the leather obtained by tanning with this material is characterized by an excellent fullness.

Example 3

100 parts of waste lye plus 5 parts hydrochloric acid are intensively stirred, then admixing 5 parts of thiourea. The condensation by means of 10 parts formaldehyde is effected in an autoclave at a pressure corresponding to 110° to 120° C and is finished after 2½ to 3 hours. The resulting tanning material is water-soluble and produces a stiff sole leather.

Example 4

	Parts
Waste lye	100
Formic acid	5
Oxypyridine	5
Formaldehyde	10

are brought together and treated as under 3.

Example 5

100 parts waste lye and 5 parts of formic acid are intensively stirred together. 10 parts cresol are stirred up and mixed until a clear solution is obtained. The mixture is then condensed with 10 parts of formaldehyde. The resulting water-soluble tanning material gives an excellent leather.

Example 6

	Parts
Waste lye	100
Lactic acid	5
Thiocresol	5
Formaldehyde	10

are brought together and treated in the manner set forth under Example 3.

Example 7

	Parts
Waste lye	100
Formic acid	5
Naphtol	5
Formaldehyde	10

are brought together and treated in the manner set forth under Example 5.

Example 8

	Parts
Waste lye	100
Glycol acid	5
Urea	5
Dextrine	10
Formaldehyde	10

are brought together and treated in the manner set forth under Example 2.

Example 9

100 parts of waste lye or acidulated with 5 parts of glycol acid and condensed by means of a reflux cooler with a mixture consisting of 10 parts of pyrogallol and 5 parts of formaldehyde, at 90° to 100° C. The resulting tanning material is readily soluble in water and produces a leather similar to Quebracho.

Example 10

100 parts waste lye are acidulated with 5 parts of formic acid and treated as under Example 5. The resulting tanning material is mixed with cresolsulphonic sodium in a proportion of 4:1. The resulting tanning material furnishes a leather similar to that produced by Quebracho tanning material, but having an almost white colour.

Example 11

100 parts of waste lye are heated with 5 parts of formic acid for 30 minutes to 50° to 60° C. 10 parts of cresol and 8 parts of acetone are admixed with continuous stirring and the mixture is treated by means of a reflux cooler for a period of 3 hours, at 80° to 90° C. The tanning material produced in this manner is fully soluble in water.

Example 12

	Parts
Waste lye	100
Formic acid	5
Cresol	5
Formaldehyde	3
Acetone	2

are mixed together and treated as described in Example 11.

Example 13

100 parts of waste lye are heated to 60° C. 10 parts of resorcin and 5 parts of formaldehyde are admixed with continuous stirring. The mixture is treated by means of a reflux cooler for a period of 4 hours at 80° to 90° C. The resulting tanning material is water-soluble and produces a soft leather.

The waste lye has a strength of 30° to 40° Baumé, advantageously of 38° Bé, and a calcium content of about 1 percent. However, waste lyes having a different calcium content, for example, up to 3 percent calcium, may also be used.

The formaldehyde referred to in the Examples has commercial strength, i. e., about 30 to 40 percent.

The acids referred to in the Examples are formic acid of 50 percent strength, lactic acid of 80 percent strength, glycol acid of 80 percent strength and hydrochloric acid of 36 percent strength, respectively. All proportions in the Examples are by weight.

The method and product of the present invention have been described in detail with reference to specific embodiments. It is to be understood, however, that the invention is not limited by such specific reference but is broader in scope and capable of other embodiments than those specifically described.

J. SEIDEL.
HELMUT WEBER.

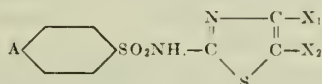
ALIEN PROPERTY CUSTODIAN

SULPHONAMIDE DERIVATIVES

Zoltán Földi, Árpád Gerecs, István Demjén, and
Rezső König, Budapest, Hungary; vested in the
Alien Property Custodian

No Drawing. Application filed April 10, 1941

The present invention relates to new 2-amino-thiazole-derivatives of anticoccic action, as well as new 2-amino-thiazole-derivatives, which are suitable starting materials to prepare new 2-amino-thiazole derivatives of anticoccic action. These derivatives have the following general formula:



in which A represents a member of the group consisting of amino-, alkylamino-, acylamino, acylated alkylamino groups and X_1 and X_2 represents a member of the group consisting of H-, alkyl-, oxoalkyl, at least one of the groups X_1 , X_2 being an oxoalkyl group.

Valuable starting materials are the acylamino-arylsulpho-thioureas, as well as the thioureaides of heterocyclic aminosulphonic acids, such as the acylamino-pyridine-sulphonyl-thiourea.

Arylsulphonyl derivatives of the thiourea have been unknown till yet, especially such arylsulphonyl-thioureas or thioureaides of heterocyclic sulphonic acids, in which the aryl group or the heterocyclic nucleus contains amino or substituted or acylated amino groups, or other groups which are convertible into the groups enumerated before. The thiourea can not be, namely acylated by acylating agents generally used for introduction of arylsulphonyl groups, because reactions of other course take place. Processes must have been created, thus, in order to obtain the starting materials of the present invention. These new starting materials can be obtained by splitting off α -alkoxy-alkyl group from the S-/ α -alkoxy-alkyl/ethers of the iso-thiourea acylated by an aromatic or heterocyclic sulphonic acid group. The starting materials for the latter process were as well unknown till yet. These starting materials can be obtained by subjecting iso-thiourea-ethers to the action of acylating agents suitable to introduce arylsulphonic groups or heterocyclic sulphonic acid groups. Such acylating agents are e. g. the arylsulpho halogenides, especially those, in which the aryl group is substituted by amino, alkylamino, acylamino groups or groups (such as nitro, azo, etc. groups) convertible into the groups mentioned before.

Such acylating agents are e. g. the acylamino-benzol-sulpho-halogenides, such as the p-acetyl-amino-benzolsulphonyl chloride. Pyridine-sulphonyl halogenides can be used as well, e. g. the 2-acetamino-pyridine-5-sulphonyl bromide. One may use, preferably, as iso-thiourea-ethers the

α -alkoxy-alkyl-ethers, such as the α -ethoxy-ethylether or, in the first place, the alkoxy-methyl-ethers, such as the methoxy-methyl or ethoxy-methyl ethers. These iso-thiourea-alkoxy-methyl ethers are preferably used in the form of their salts, as the free bases themselves are unstable. When using the salts, it is preferable to use acid binding agents, such as pyridine, sodium acetate, sodium alcoholate, etc.

Further details of the process for the obtention of arylsulpho-iso-thiourea-ethers are to be found in the examples.

The removal of the alkoxy-alkyl group from the aryl-sulpho-iso-thiourea ethers can be, preferably, effected by alcoholysis. For this splitting off specially those arylsulpho-iso-thiourea-alkyl ethers are suitable in which the alkyl group is an alkoxy-methyl or phenoxy-methyl group, preferably an ethoxy-methyl or methoxy-methyl group. The alcoholysis is effected, preferably, in the presence of acid catalysts, such as dry hydrochloric acid. The alcoholysis is effected in an absolute alcohol, containing 0.1-0.3 percent of dry hydrochloric acid. As alcohol, the methyl- or ethyl-alcohol can be advantageously used. The alkoxy-methyl groups are split off by this alcoholysis in form of acetals of the formaldehyde. As starting materials for this hydrolysis acylamino-arylsulpho- or nitro-aryl-sulpho-iso-thiourea-alkoxy-methyl ethers can be preferably used.

Further details of the alcoholysis are to be found in the examples.

As other components for the process of the present invention are α -halogene derivatives of di-ketones or poly-ketones, such as the chloro- or bromo-acetyl-acetone symmetric, the bromo-di-acetyl-monoxime.

The reaction between the arylsulpho-thiourea and the α -halogenated oxo-compound is preferably carried out in the presence of an acid binding agent, such as of pyridine or other tertiary heterocyclic bases.

Further details concerning the preparation of the starting materials and of the end-products are to be found in the examples.

(1.) Thiourea and chloro-methylether are brought into interaction in acetone at room-temperature. The hydrochloride of the iso-thiourea-methoxy-methyl-ether separates. It melts at about 102°.

300 ccs of absolute methylalcohol are cooled to -10° and 62.4 grams of chlorhydrate of iso-thiourea-methoxy-methylether are added. While stirring the hydro-chloride dissolves. Now a sodium-methylate solution is added in portion at

—10°. The sodium-methylate solution has been prepared from 8.5 grams of sodium and 300 ccs of absolute methylalcohol. After the sodium-methylate solution has been added, 42 grams of finely powdered p-acetamino-benzol-sulpho-chloride are added in portions at —10°, while stirring. The stirring is continued at —10°, then for about one hour at about 0°. The p-acetamino - benzolsulpho - iso - thiourea - methoxy - methylether separates as a crystal mass. It is now filtered, the precipitate washed with water in order to eliminate the sodium chloride, then dried. One obtains about 40 grams of a white crystalline product, which melts at about 167°. It can be recrystallised from alcohol.

One may prepare similarly the corresponding products, starting from benzolsulpho-chloride or from p-nitro-benzolsulpho-chloride or from 2-acetamino-pyridine-5-sulphonyl bromide.

(2.) 37.6 grams of finely powdered p-acetyl-amino - benzol - sulpho - iso - thiourea-methoxy-methylether are boiled for a minute in 222 ccs of 99% methyl-alcohol and 1.1 ccs of absolute ethyl-alcohol, containing 33% hydrochloric acid gas. The starting material passes into solution and crystallisation occurs soon. The mixture is boiled for further 2 minutes, then allowed to cool, then cooled by ice-water. The crystals are filtered. One obtains 25–28 grams of p-acetyl-amino-benzolsulpho-thiourea, as a white crystalline powder, which melts at about 200.5°. It dissolves in diluted alcohol and can be reprecipitated without alteration by acidification with acetic acid.

The splitting off of the methoxy-methyl group can be effected also in ethylalcoholic medium. Instead of the methoxy-methyl-ether of the p-acetamino-benzolsulpho-iso-thiourea, one may use the ethoxymethylether or the α -ethoxy-ethyl-ether as well. Instead of the p-acetamino-benzolsulpho-iso-thiourea ethers one may use the corresponding p-nitro-benzolsulpho-iso-thiourea ethers. One obtains, in this case, the p-nitro-benzolsulpho-thiourea. From 2-acetamino-pyridine - 5 - sulpho-iso-thiourea-methoxy-methyl-ether one obtains the 2-acetamino-pyridine-5-sulpho-thiourea.

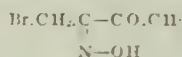
(3.) 2.7 grams of mono-chloro-acetylacetone symmetric, 5.5 grams of p-acetyl-amino-benzol-

sulpho-thiourea and 6 ccs of dry pyridine are mixed. A violent reaction takes place. The pale yellow melted mixture solidifies in crystals, on standing. After addition of 40 ccs of water it is ground and suctioned and washed by water. One obtains, in theoretical amount, the 2-(p-acetamino-benzol-sulphamido)-4-methyl-5-aceto-thiazole, which does not melt till 280°.

2.5 grams of this product are boiled in 20 ccs of sodium hydroxide of 10 volume % and in 5 ccs of water. The pale yellow solution is acidified by 2.5 ccs of glacial acetic acid. The precipitate is filtered, washed by water and dried. The product is boiled with 9 ccs of absolute alcohol, then cooled and filtered. One obtains the 2-(p-amino-benzolsulphamido)-4-methyl-5-aceto-thiazole, which melts at 213–14°.

The same product can be obtained by condensing mono-chloro-acetylacetone with p-amino-benzolsulpho-thiourea.

(4.) 3.6 grams of the mono-bromo-diacetyl-monoxime according to the formula:



and 5.5 grams of p-acetamino-benzolsulpho-thiourea and 6 ccs of dry pyridine are mixed. Under elevation of temperature a yellowish melt is formed, which is kept some minutes on the water-bath, then cooled and additioned by 20 ccs of water. On cooling and standing white crystals separate, which are suctioned and washed by water. One obtains the 2-(p-acetyl-amino-benzolsulphamido)-4-aceto-thiazole-oxime, which melts at about 204°. It dissolves readily in $\frac{1}{2}$ -normal sodium hydroxide.

On splitting off the acetyl group as well as the hydroxylamine by hydrolysis, one obtains the corresponding 4-aceto-derivative.

The experimental conditions given in the examples can be varied in many other respects as well.

ZOLTÁN FÖLDI.
ÁRPÁD GERECS.
ISTVÁN DEMJÉN.
REZSŐ KÖNIG.

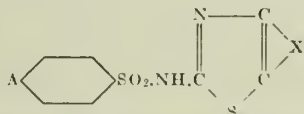
ALIEN PROPERTY CUSTODIAN

SULPHONAMIDE DERIVATIVES

Zoltán Földi, Árpád Gerecs, István Demjén, and
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No Drawing. Application filed April 10, 1941

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in which A represents a member of the group consisting of amino-, alkylamino-, acylamino-, acylated alkylamino groups and X represents a bivalent aliphatic hydrocarbon chain, containing at least three carbon atoms. The bivalent group X can preferably be a tetramethylene chain which can wear a hydrocarbon side chain.

Valuable starting materials are the acylamino-arylsulpho-thioureas, as well as the thioureides of heterocyclic aminosulphonic acids, such as the acylamino-pyridine sulphonyl-thiourea.

Arylsulphonyl derivatives of the thiourea have been unknown till yet, especially such arylsulphonyl-thioureas or thioureides of heterocyclic sulphonic acids, in which the aryl group or the heterocyclic nucleus contains amino or substituted or acylated amino groups, or other groups which are convertible into the groups enumerated before. The thiourea can not be, namely, acylated by acylating agents generally used for introduction of arylsulphonyl groups, because reactions of other course take place. Processes must have been created, thus, in order to obtain the starting materials of the present invention. These new starting materials can be obtained by splitting off α -alkoxy-alkyl group from the S-(α -alkoxy-alkyl)-ethers of the iso-thiourea acylated by an aromatic or heterocyclic sulphonic acid group. The starting materials for the latter process were as well unknown till yet. These starting materials can be obtained by subjecting iso-thiourea-ethers to the action of acylating agents suitable to introduce arylsulphonic groups or heterocyclic sulphonic acid groups. Such acylating agents are e. g. the arylsulpho halogenides, especially those, in which the aryl group is substituted by amino, alkylamino, acylamino groups or groups (such as nitro, azo, etc. groups) convertible into the groups mentioned before.

Such acylating agents are e. g. the acylamino-benzol-sulpho-halogenides, such the p-acetyl-amino-benzol-sulphonyl chloride. Pyridine-sulphonyl halogenides can be used as well, e. g. the

2-acetamino-pyridine-5-sulphonyl bromide. One may use, preferably, as iso-thiourea-ethers the α -alkoxy-alkyl-ethers, such as the α -ethoxy-ethylether or, in the first place, the alkoxy-methyl-ethers, such as the methoxy-methyl or ethoxy-methyl ethers. These iso-thiourea-alkoxy-methyl ethers are preferably used in the form of their salts, as the free bases themselves are unstable. When using the salts, it is preferable to use acid binding agents, such as pyridine, sodium acetate, sodium alcoholate, etc.

Further details of the process for the obtaining of arylsulpho-iso-thiourea-ethers are to be found in the examples.

The removal of the alkoxy-alkyl group from the aryl-sulpho-iso-thiourea ethers can be, preferably, effected by alcoholysis. For this splitting off specially those aryl-sulpho-iso-thiourea-alkyl ethers are suitable in which the alkyl group is an alkoxy-methyl or phenoxy-methyl group, preferably an ethoxy-methyl or methoxy-methyl group. The alcoholysis is effected, preferably, in the presence of acid catalysts, such as dry hydrochloric acid. The alcoholysis is effected in an absolute alcohol, containing 0.1-0.3 percent of dry hydrochloric acid. As alcohol, the methyl- or ethyl-alcohol can be advantageously used. The alkoxy-methyl groups are split off by this alcoholysis in form of acetals of the formaldehyde. As starting materials for this hydrolysis acyl-amino-arylsulpho- or nitro-aryl-sulpho-iso-thiourea-alkoxy-methyl ethers can be preferably used.

Further details of the alcoholysis are to be found in the examples.

As other components for the process of the present invention are the α -halogen derivatives of cyclic ketones, such as the α -chloro-cyclohexanone or 2-chloro-methyl-cyclo-hexanones.

The reaction between the arylsulpho-thiourea and the α -halogenated oxo-compound is preferably carried out in the presence of an acid binding agent, such as of pyridine or other tertiary heterocyclic bases.

Further details concerning the preparation of the starting materials and of the end-products are to be found in the examples.

(1.) Thiourea and chloro-methylether are brought into interaction in acetone at room-temperature. The hydrochloride of the iso-thiourea-methoxy-methyl-ether separates. It melts at about 102°.

300 ccs of absolute methylalcohol are cooled to -10° and 62.4 grams of chlorhydrate of iso-thiourea-methoxy-methylether are added. While

stirring the hydro-chloride dissolves. Now a sodium-methylate solution is added in portion at -10° . The sodium-methylate solution has been prepared from 8.5 grams of sodium and 300 ccs of absolute methylalcohol. After the sodium-methylate solution has been added, 42 grams of finely powdered p-acetamino-benzolsulphochloride are added in portions at -10° , while stirring. The stirring is continued at -10° , then for about one hour at about 0° . The p-acetamino-benzolsulpho-iso-thiourea-methoxy-methylether separates as a crystal mass. It is now filtered, the precipitate washed with water in order to eliminate the sodium chloride, then dried. One obtains about 40 grams of a white crystalline product, which melts at about 167° . It can be recrystallised from alcohol.

One may prepare similarly the corresponding products, starting from benzolsulpho-chloride or from p-nitro-benzolsulpho-chloride or from 2-acetamino-pyridine-5-sulphonyl bromide.

(2.) 37.6 grams of finely powdered p-acetyl-amino - benzol - sulpho - iso-thiourea-methoxy-methylether are boiled for a minute in 222 ccs of 99% methyl-alcohol and 1.1 ccs of absolute ethyl-alcohol, containing 33% hydrochloric acid gas. The starting material passes into solution and crystallisation occurs soon. The mixture is boiled for further 2 minutes, then allowed to cool, then cooled by ice-water. The crystals are filtered. One obtains 25-28 grams of p-acetyl-amino-benzolsulpho-thiourea, as a white crystalline powder, which melts at about 200.5° . It dissolves in diluted alcohol and can be reprecipitated without alteration by acidification with acetic acid.

The splitting off of the methoxy-methyl group can be effected also in ethylalcoholic medium. Instead of the methoxy-methyl-ether of the p-acetamino-benzol-sulpho-iso-thiourea, one may use the ethoxymethylether or the α -ethoxy-ethyl-ether as well. Instead of the p-acetamino-benzolsulpho-iso-thiourea ethers one may use the corresponding p-nitro-benzolsulpho-iso-thiourea ethers. One obtains, in this case, the p-nitro-benzol-sulpho-thiourea. From 2-acet-amino-pyridine - 5 - sulpho-iso-thiourea-methoxy-methylether one obtains the 2-acetamino-pyridine-5-sulpho-thiourea.

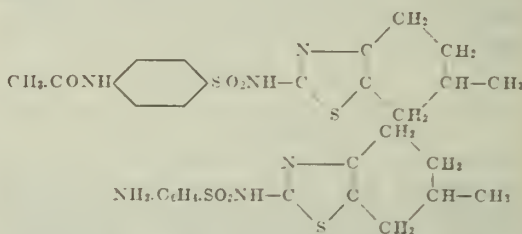
(3.) 132 grams of α -chloro-cyclohexanon, 273

grams of p-acetamino-benzolsulpho-thiourea and 300 ccs of dry pyridine are stirred and warmed on the water-bath. The reaction components go into solution. Then the mixture is cooled and the thick syrup is mixed with 2 litres of water. An oil separates, which crystallises soon. After standing the crystals are filtered, washed and dried. For further purification they can be crystallised from large amounts of hot alcohol of 90%. One obtains the 4,5-tetramethylene-2-(p-acetyl-amino-benzolsulphamido)-thiazole, which melts at about $265-280^{\circ}$.

This product, boiled with the eightfold amount of sodium hydroxyde of 10 volume % for half an hour and then acidified by hydrochloric acid, yields the 4,5-tetramethylene-2-(p-amino-benzolsulphamido)-thiazole, melting at about 244° . The product has antiseptic action.

When using, instead of p-acetyl-amino-benzolsulpho-thiourea, the p-amino-benzolsulpho-thiourea. One obtains directly the product described above.

One may obtain similarly from 2-chloro-methyl-cyclo-hexanon the compounds of the formula:



Starting from the cyclic α -halogeno-ketones mentioned in this example and condensing them with p-nitro-benzolsulpho-thiourea or with benzolsulpho-thiourea, one obtains the corresponding nitrobenzol-sulphonyl- or benzolsulphonyl-amino-thiazole derivatives.

The experimental conditions given in the examples can be varied in many other respects as well.

ZOLTÁN FÖLDI.
ÁRPÁD GERECS.
ISTVÁN DEMJÉN.
REZSŐ KÖNIG.

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SULPHONAMIDE DERIVATIVES

Zoltán Földi, Árpád Gerecs, István Demjén, and
Rezső König, Budapest, Hungary; vested in the
Alien Property Custodian

No Drawing. Application filed April 10, 1941

The present invention relates to new 2-amino-thiazole-derivatives of anticoccic action, as well as new 2-amino-thiazole derivatives, which are suitable starting materials to prepare new 2-amino-thiazole derivatives of anticoccic action. These derivatives are, 2-arylsulphamido-4-oxy-thiazoles, in which the aryl-group contains in the para-position a member of the group consisting of: amino-, acylamino-, alkyl- amino-, acylated alkylamino-, nitro-groups, as substitu-

ent. Valuable starting materials are the acylamino-aryl-sulpho-thioureas, as well as the thioureides of heterocyclic aminosulphonic acids, such as the acylamino-pyridine-sulphonyl-thiourea.

Arylsulphonyl derivatives of the thiourea have been unknown till yet, especially such arylsulphonyl-thioureas or thioureids of heterocyclic sulphonic acids, in which the aryl group or the heterocyclic nucleus contains amino or substituted or acylated amino groups, or other groups which are convertible into the groups enumerated before. The thiourea can not be, namely, acylated by acylating agents generally used for introduction of arylsulphonyl groups, because reactions of other course take place. Processes must have been created, thus, in order to obtain the starting materials of the present invention. These new starting materials can be obtained by splitting off α -alkoxy-alkyl group from the S-(α -alkoxy-alkyl)-ethers of the iso-thiourea acylated by an aromatic or heterocyclic sulphonic acid group. The starting materials for the latter process were as well unknown till yet. These starting materials can be obtained by subjecting iso-thiourea-ethers to the action of acylating agents suitable to introduce arylsulphonic groups or heterocyclic sulphonic acid groups. Such acylating agents are e.g. the arylsulpho halogenides, especially those, in which the aryl group is substituted by amino, alkylamino, acylamino groups or groups (such as nitro, azo, etc. groups) convertible into the groups mentioned before.

Such acylating agents are e. g. the acylamino-benzol-sulpho-halogenides, such as the p-acetyl-amino-benzolsulphonyl chloride. Pyridine-sulphonyl halogenides can be used as well, e.g. the 2-acetamino-pyridine-5-sulphonyl bromide. One may use, preferably, as iso-thiourea-ethers the α -alkoxy-alkyl-ethers, such as the α -ethoxy-ethylether or, in the first place, the alkoxy-methyl-ethers, such as the methoxy-methyl or ethoxy-methyl ethers. These iso-thiourea-alkoxy-methyl ethers are preferably used in the form of their salts, as the free bases themselves

are unstable. When using the salts, it is preferably to use acid binding agents, such as pyridine, sodium acetate, sodium alcoholate, etc.

Further details of the process for the obtention of arylsulpho-iso-thiourea-ethers are to be found in the examples.

The removal of the alkoxy-alkyl group from the aryl-sulpho-iso-thiourea ethers can be, preferably, effected by alcoholysis. For this splitting off specially those arylsulpho-iso-thiourea-alkyl ethers are suitable in which the alkyl group is an alkoxy-methyl or phenoxy-methyl group, preferably an ethoxy-methyl or methoxy-methyl group. The alcoholysis is effected, preferably, in the presence of acid catalysts, such as dry hydrochloric acid. The alcoholysis is effected in an absolute alcohol, containing 0.1-0.3 percent of dry hydrochloric acid. As alcohol, the methyl- or ethyl-alcohol can be advantageously used. The alkoxy-methyl groups are split off by this alcoholysis in form of acetates of the formaldehyde. As starting materials for this hydrolysis acylamino-arylsulpho- or nitro-aryl-sulpho-iso-thiourea-alkoxy-methyl ethers can be preferably used.

Further details of the alcoholysis are to be found in the examples.

As other components for the process of the present invention are the α -halogenated acids or its ethers or α -halogenated derivatives of di- or poly-carboxylic acids or of their esters. Such compounds are e. g. the chloro-acetic acid, the chloroacetic acid ethylester, the bromo- or chloro-malonic acid diethyl ester, the chloro-cyan-acetic-acid-ester, etc.

The reaction between the arylsulpho-thiourea and the α -halogenated oxo-compound is preferably carried out in the presence of an acid binding agent, such as of pyridine or other tertiary heterocyclic bases.

Further details concerning the preparation of the starting materials and of the end-products are to be found in the examples.

(1.) Thiourea and chloro-methylether are brought into interaction in acetone at room-temperature. The hydrochloride of the iso-thiourea-methoxy-methyl-ether separates. It melts at about 102°.

300 ccs of absolute methylalcohol are cooled to -10° and 62.4 grams of chlorhydrate of iso-thiourea-methoxy-methylether are added. While stirring the hydro-chloride dissolves. Now a sodium-methylate solution is added in portion at -10°. The sodium-methylate solution has been prepared from 8.5 grams of sodium and 300 ccs

of absolute methylalcohol. After the sodium-methylate solution has been added, 42 grams of finely powdered p-acetamino-benzolsulpho-chloride are added in portions at -10° , while stirring. The stirring is continued at -10° , then for about one hour at about 0° . The p-acetamino-benzolsulpho-iso-thiourea-methoxy-methylether separates as a crystal mass. It is now filtered, the precipitate washed with water in order to eliminate the sodium chloride, then dried. One obtains about 40 grams of a white crystalline product, which melts at about 167° . It can be recrystallised from alcohol.

One may prepare similarly the corresponding products, starting from benzolsulpho-chloride or from p-nitro-benzolsulpho-chloride or from 2-acetamino-pyridine-5-sulphonyl bromide.

(2.) 37.6 grams of finely powdered p-acetyl-amino-benzol - sulpho - iso - thiourea - methoxy - methylether are boiled for a minute in 222 ccs of 99% methyl-alcohol and 1.1 ccs of absolute ethyl-alcohol, containing 33% hydrochloric acid gas. The starting material passes into solution and crystallisation occurs soon. The mixture is boiled for further 2 minutes, then allowed to cool, then cooled by ice-water. The crystals are filtered. One obtains 25-28 grams of p-acetyl-amino-benzolsulpho-thiourea, as a white crystalline powder, which melts at about 200.5° . It dissolves in diluted alcohol and can be reprecipitated without alteration by acidification with acetic acid.

The splitting off of the methoxy-methyl group can be effected also in ethylalcoholic medium. Instead of the methoxy-methyl-ether of the p-acetamino-benzolsulpho-iso-thiourea, one may use the ethoxy-methyl-ether or the α -ethoxy-ethylether as well. Instead of the p-acetamino-benzolsulpho-iso-thiourea ethers one may use the corresponding p-nitro-benzolsulpho-iso-thiourea ethers. One obtains, in this case, the p-nitro-benzol-sulpho-thiourea. From 2-acet-amino-pyridine-5-sulpho-iso-thiourea-methoxy-methyl-ether one obtains the 2-acetamino-pyridine-5-sulpho-thiourea.

(3.) 7.5 grams of ethyl chloro-acetate, 16.5 grams of p-acetamino-benzolsulpho-thiourea and 18 ccs of pyridine are mixed. The temperature rises to about 40° and a dissolution occurs. After heating on the waterbath for about a quarter of an hour, the mixture is diluted by 150 ccs of water, upon which the p-acetyl-amino-benzol-sulpho-2-amino-4-oxy-thiazole separates as a crystalline powder. The yield is about 75% of the theory. It decomposes at $258-59^{\circ}$.

(4.) 12.5 grams of ethyl chloro-acetate, 23

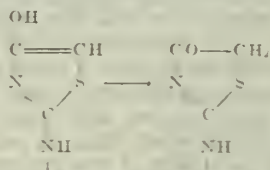
grams of p-amino-benzolsulpho-thiourea and 30 ccs of pyridine are mixed. A slight elevation of the temperature takes place and materials go into solution. The mixture is then heated on water-bath for half an hour, then diluted by 150 ccs of warm water. On cooling the p-amino-benzol-sulpho-2-amino-4-oxy - thiazole crystallises in compact crystals, melting at $235-37^{\circ}$. The yield is about 60% of the theory.

(5.) 4 grams of chloro-malonic diethyl ester, 5.5 grams of p-acetamino-benzolsulpho-thiourea and 6 ccs of pyridine are mixed, then heated at about 60° for a quarter of an hour. One obtains a homogeneous yellow syrup, which solidifies after standing for 2 hours. On addition of 70 ccs of water, the crystals dissolve, followed soon by precipitation of white crystals. One obtains 7.05 grams of crystals, melting at 164° under development of gas. The product is recrystallisable from alcohol, the melting point rising thus to $165-166^{\circ}$. The product is the 4-oxy-derivative of p-acetamino - benzol - sulpho-2-amino-5-carbethoxy-thiazole.

(6.) 4.8 grams of bromo-malonic diethylester, 4.6 grams of p-amino-benzol-sulpho-thiourea and 6 ccs of pyridine are mixed upon which the temperature rises to about 75° . The yellow thick syrup thus formed, is heated on the waterbath for 10 minutes, then allowed to stand for an hour and a half, and then diluted by 80 ccs of water. The homogeneous solution deposits 5.9 grams of pale yellow crystals, which melt between $136-138^{\circ}$. This product recrystallised from alcohol melts at $138-139^{\circ}$, under decomposition. The product is the deacetylated derivative of the product described in the preceding example.

The experimental conditions given in the examples can be varied in many other respects as well.

As well known, 4-oxy-thiazoles show a tautomerism between the two following formulas:



In the present invention a nomenclature according to the left-hand formula has been chosen.

ZOLTÁN FÖLDI.
ÁRPÁD GERECS.
ISTVÁN DEMJÉN.
REZSŐ KÖNIG.

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PRODUCTION OF SUPERPOLYAMIDES

Heinrich Hopff and Hanns Ufer, Ludwigshafen-on-Rhine, and Max Conrad, Leverkusen-I. G. Werk, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 17, 1941

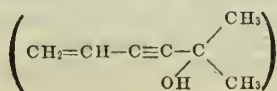
The present invention relates to a process for the production of superpolyamides.

Superpolyamides, i. e. condensation products similar to polypeptides which can be drawn into threads, are obtained by condensing diamines with approximately equimolecular proportions of dicarboxylic acids or of functional derivatives of the said acids capable of forming amides, or by condensing salts of diamines with dicarboxylic acids, or by condensing aminocarboxylic acids or their functional derivatives capable of forming amides, while operating at an elevated temperature, for example between 200 and 300°, preferably between 250 and 280 to 290° C. By a proper selection of the initial materials and the use of mixtures of the single components, the properties of the final products may be varied within wide limits.

We have now found that superpolyamides having especially valuable properties are obtained by adding to the diamines and dicarboxylic acids or their functional derivatives capable of forming amides or the salts of diamines with dicarboxylic acids or the aminocarboxylic acids to be condensed less than 10 per cent, preferably up to 2 per cent by weight, of aliphatic or cycloaliphatic carboxylic acids containing at least 3 carboxylic groups, or of aliphatic or cycloaliphatic compounds containing at least one hydroxyl group and in addition at least 2 further hydroxyl groups or unsaturated linkages, advantageously in conjunction with polybasic (including dibasic) carboxylic acids.

Suitable carboxylic acids containing at least 3 carboxylic groups are, for example, ethane-, propane-, butane-, hexanetri- or -tetracarboxylic acid and cyclohexanone-1.1.1'.1'-tetracarboxylic acid. These acids are preferably added only in slight proportions, advantageously less than 2 per cent, in order to procure products with a sufficient length of chain. The said polycarboxylic acids can be employed in combination with diamines or polyamines, either in the form of their salts or in admixture with such amines.

Among compounds containing at least one hydroxyl group and, besides, two further hydroxyl groups or unsaturated linkages, we may mention trihydric alcohols or alcohols of a higher valency, as for example glycerine, trimethylolethane, trimethylol-propane or hexanetriol, or compounds of the type of vinyl ethinyl-dimethylcarbinol



A preferred method of practising the process according to the present invention consists in adding trihydric alcohols or alcohols of a higher valency together with dibasic acids or acids of higher basicity. Acids containing more than two carboxylic groups, when used together with higher than dihydric alcohols, should be employed in an amount which together with the amount of the said alcohols is less than 10 per cent (by weight) of the bifunctional substances forming the superpolyamides. Instead of the said alcohols and the said acids of either the dibasic or higher-basic type, there may also be employed products of the alkyd resin type of low degree of condensation prepared therefrom. By the addition of the at least tri-valent alcohols together with di- or higher-basic acids or condensation products thereof, greater stiffness and hardness are imparted to the final product without its further good mechanical properties being deteriorated. Such products are especially adapted to the manufacture of stiff articles by injection-molding and the manufacture of stiff bristles. The influence of the said additions on the properties of the products depends on the proportions of the substances added. While additions of more than 10 per cent generally will yield infusible and completely insoluble products, additions of less than 10, preferably less than 2, per cent are very advantageous. The properties of the products can be influenced also by the quantitative relation between the tri- or higher-valent alcohols and the di- or higher-basic acids (exceeding the amount of dicarboxylic acid required for the amide formation). Usually it is of advantage to use more alcohol than can be esterified by the quantity of acid added. The said compounds containing more than 2 functional groups exert a stabilizing action on the products.

The said substances are usually added to the basic materials forming the superpolyamides in the very outset of the operation; alternatively, they may also be added after the materials forming the superpolyamides have undergone already partial condensation.

As starting materials for the production of the superpolyamides may be mentioned, for example, the usual diamines, as for example penta-, hexa-, dekamethylenediamine and the like, and dicarboxylic acids, as for example maleic acid, glutaric acid, adipic acid, pimelic acid, sebacic acid, phthalic acid and terephthalic acid in admixture with one another or in the form of their salts, furthermore the usual aminocarboxylic acids, as for example ϵ -aminocaproic acid. These compounds can also be employed in the form of suit-

able functional derivatives, for example the aminocarboxylic acids can be used in the form of their lactams.

The condensation is carried out in the manner usual in the manufacture of superpolyamides, under increased, atmospheric or reduced pressure and, if desired, in the presence of water or solvents. When the operation is nearing its end, the water must be eliminated.

The following Examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to these Examples. These parts are by weight.

Example 1

2000 parts of the adipic acid salt of hexamethylenediamine, 1000 parts of water, 14.6 parts of adipic acid and 15 parts of trimethylol propane are slowly heated in a pressure-tight vessel up to from 275 to 280° C in an atmosphere of nitrogen free from oxygen, the pressure being maintained at 15.0 atmospheres by releasing the steam evolved in the reaction. When the temperature has been raised to 275–280° C, the pressure is lowered down to atmospheric pressure within 1½ hours and the condensation is completed by heating for another 1½ hours under atmospheric pressure. By introducing the melt into water a white, hard and stiff condensation product is obtained, from which extremely hard and stiff materials of very good mechanical strength are obtained, by working up for example by injection-molding.

Similar products are obtained if 21.0 parts of trimethylol propane are employed instead of 15.0 parts under otherwise identical conditions.

In the case of smaller additions of adipic acid and trimethylol propane condensation products are obtained, the hardness and stiffness of which shows a somewhat slighter increase as compared with a superpolyamide obtained from adipic acid and hexamethylenediamine alone; when adding larger amounts of adipic acid and trimethylol propane, for example more than 5 per cent, the products likewise show a high stiffness and hardness, but their strength is a little lessened.

Example 2

1000 parts of the adipic acid salt of hexamethylenediamine, 500 parts of water, 7.1 parts of adipic acid and 8.1 parts of a crude mixture mainly consisting of hexanetriol and some octanetetrol (obtained as a residue in the distillation of 1,3-butyleneglycol formed by the hydrogenation of aldol) are treated in the manner indicated in Example 1. The condensation product obtained is distinguished by its high stiffness and hardness and very good strength.

Example 3

A mixture of 1000 parts of the adipic acid salt of hexamethylenediamine, 500 parts of water, 7.5 parts of adipic acid and 10.5 parts of trimethylol-ethane is treated in the manner indicated in Example 1. A white product is obtained which possesses great strength and is very well suited, for example, for the manufacture of bristles.

Example 4

2000 parts of ε-aminocaproic acid lactam (briefly referred to in the following Examples as ε-caprolactam), 15 parts of adipic acid and 21 parts of trimethylol propane are condensed in the presence of water in the manner indicated in Example 1. The product so obtained is consid-

erably harder and stiffer than a condensation product of the lactam alone. It is especially suited for producing bristles.

Example 5

1500 parts of ε-caprolactam and 19.1 parts of 1,2,3,4-butanetetracarboxylic acid are condensed in the presence of 450 parts of water in the manner indicated in Example 1. A colorless condensation product is thus obtained which melts at 195° C and is stiffer than a condensation product to which no addition was made, but well elastic. The stiffness of condensation products from the adipic acid or sebacic acid salt of hexamethylenediamine, or of mixed condensation products of ε-caprolactam with the said salts is similarly improved by the interaction with butanetetracarboxylic acid.

Example 6

1200 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 15.51 parts of the salt from equimolecular amounts of butanetetracarboxylic acid and hexamethylenediamine and 1000 parts of water are treated under the conditions indicated in Example 1. A tough, but comparatively stiff, colorless condensation product soluble in hot methanol is thus obtained.

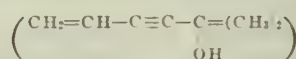
When 800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 100 parts of 1,2,3,4-butanetetracarboxylic acid and 55 parts (or 84.8 parts) of hexamethylenediamine are condensed under the same conditions, yellowish, rather stiff, elastic condensation products are obtained which are soluble in hot methanol and methylbutinol.

Example 7

1200 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 19 parts of the salt from 1 molecular proportion of cyclohexanone-1,1,1',1'-tetrapropionic acid and 2 molecular proportions of hexamethylenediamine are condensed in the presence of 1000 parts of water in the manner described in Example 1. The condensation product obtained yields a highly viscous melt.

Example 8

800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam and 16 parts of vinyl ethinyldimethylcarbinol



are treated in the manner described in Example 1. A colourless condensation product is obtained which is softer than one prepared without adding vinyl ethinyldimethylcarbinol. Films of good appearance and strength may be cast from warm aqueous methanol solutions of the product.

Example 9

800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ε-caprolactam, 11.04 parts of the salt from 2 molecular proportions of hexamethylenediamine and 1 molecular proportion of 1,2,3,4-butanetetracarboxylic acid, 4.46 parts of 1,2,3,4-butanetetracarboxylic acid and 700 parts of water are treated in the manner described in Example 1. The product obtained melts at about 180°C and may be cast to form soft, strong, practically clear films.

A similar product of somewhat greater hard-

ness is obtained when using 9.42 parts of 1.2.3.4-butanetetracarboxylic acid instead of 4.46 parts.

Example 10

800 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ϵ -caprolactam, 48 parts of vinyl ethinyldimethylcarbinol and 800 parts of water are treated in the manner described in Example 1. A solid, soft, yellowish condensation product is obtained which may readily be molded into plates. Films may be produced from its solutions.

A similar condensation product is obtained from 1200 parts of the adipic acid salt of hexamethylenediamine, 800 parts of ϵ -caprolactam, 40 to 60 parts of vinyl ethinyldimethylcarbinol and 1000 parts of water.

When 2000 parts of ϵ -caprolactam, 40 to 60 parts of vinyl ethinyldimethylcarbinol and 80 parts of water are condensed, a yellow, very soft condensation product insoluble in hot aqueous methanol is obtained.

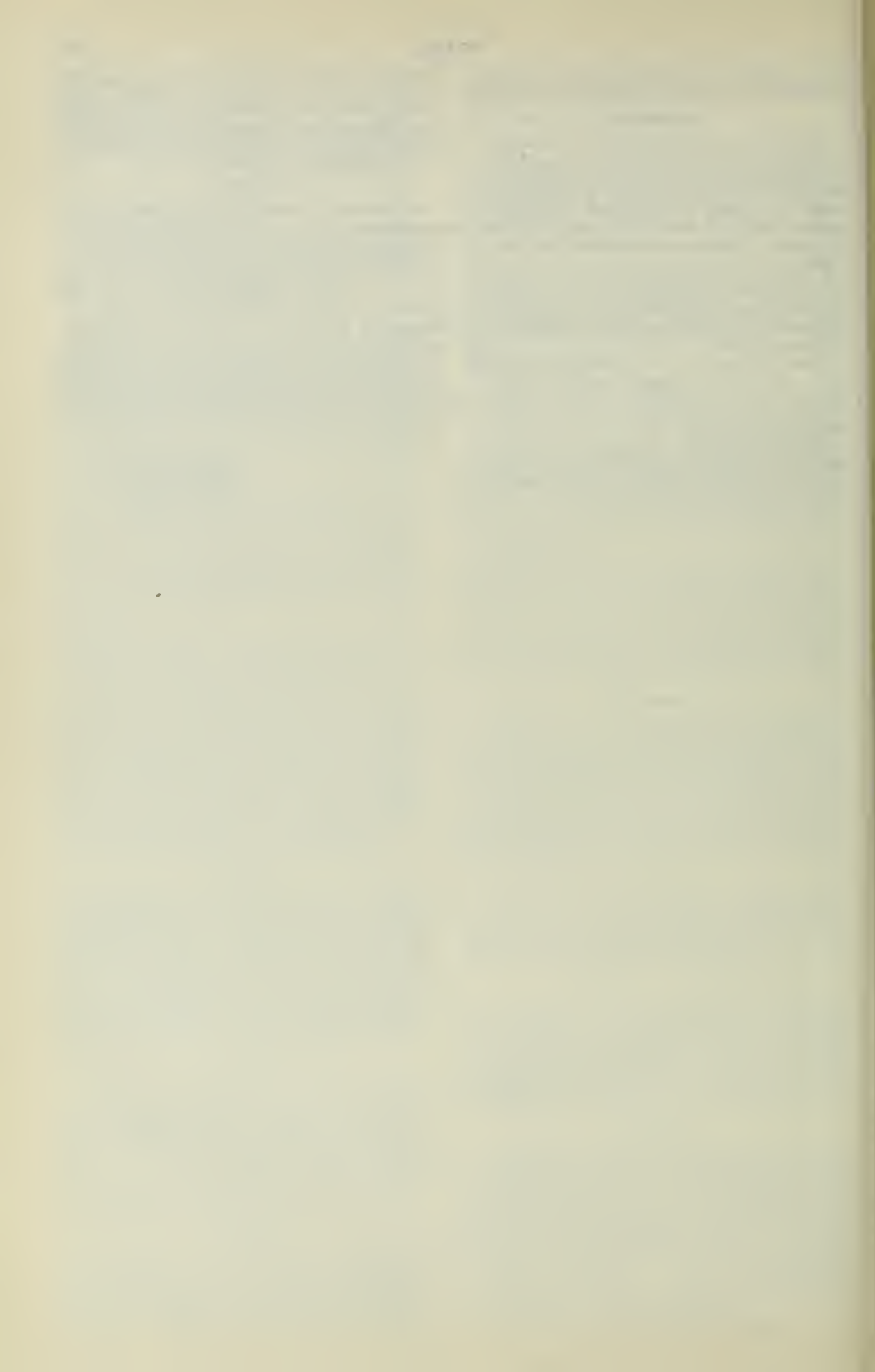
When a mixture of 2000 parts of the adipic acid salt of hexamethylenediamine, 60 parts of vinyl ethinyldimethylcarbinol and 1000 parts of water is treated in an analogous manner, a con-

densation product is obtained which is especially suitable for the production of bristles. Such bristles possess a better resilience as compared with bristles from a corresponding condensation product produced without the co-employment of vinyl ethinyldimethylcarbinol.

Example 11

500 parts of the adipic acid salt of hexamethylenediamine, 1500 parts of ϵ -caprolactam, 13.8 parts of the salt from 2 molecular proportions of hexamethylenediamine and 1 molecular proportion of 1.2.3.4-butanetetracarboxylic acid, 60 parts of vinyl ethinyldimethylcarbinol and 1000 parts of water are treated in the manner described in Example 1. An elastic condensation product of good mechanical strength is obtained. By coemploying the sebacic acid salt of hexamethylenediamine or replacing part of the adipic acid salt of hexamethylenediamine by the said sebacic acid salt or by adding 11-aminostearic acid the softness of the product is still improved.

HEINRICH HOPFF.
HANNS UFER.
MAX CONRAD.



ALIEN PROPERTY CUSTODIAN

CATALYTIC REACTIONS WITH CARBONACEOUS MATERIALS

Fritz Stoewener, deceased, late of Ludwigshafen-on-Rhine, by Hedwig Elisabeth Stoewener, administratrix, Ludwigshafen-on-Rhine, Germany, and Emil Keunecke, Ludwigshafen-on-Rhine, and Friedrich Becke, Mannheim, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 17, 1941

The present invention relates to a process of carrying out catalytic reactions with carbonaceous materials.

This application is a continuation-in-part to our application Ser. No. 321,210, filed February 28, 1940.

It is known that in certain catalytic reactions with carbonaceous materials at an elevated temperature, for example above 200° C and more, particularly above 300° C, in particular in the cracking of hydrocarbon oils or in the destructive hydrogenation of coals, tars and mineral oils porous catalysts or carriers, for catalytic substances, consisting of porous materials may be used. Solid gels of silicic acid or silicates, in particular, have already been employed for this purpose either alone or in combination with one or more metal compounds, preferably alumina. Such gels are generally distinguished by having pores of ultramicroscopic fineness. The pores of a given gel, however, are but rarely uniform in diameter; most gels rather possess pores of most diverse diameter varying for example between 0 and 50 $\mu\mu$ and above; part of the pores often exceeds even ultramicroscopic dimensions, depending on the conditions under which the gels were made. For catalytic purposes large-pored gels are usually preferred, i. e. gels the active pore volume of which is predominantly made up of pores, for example to the extent of 80 to 90 per cent, the diameter of which spreads over a range of between 2 and 43 $\mu\mu$ because such gels are especially well suited for absorbing solutions of substances having a catalytic action. The gel-like catalysts and carrier masses hitherto used in catalytic reactions with carbonaceous substances, however, left much to be desired in efficiency, as no considerations were known which might be a guide in choosing the porous masses.

The said application Ser. No. 321,210 is concerned with a process of carrying out catalytic reactions involving hydrocarbons in which porous catalysts are employed of which the active pore volume spreads, to at least 30 per cent of the pores, over diameters of between 0 and 2 $\mu\mu$.

We have found that excellent yields are obtained in this conversion, if such porous catalysts or carrier masses be used in which at least 30 per cent, preferably at least 50 per cent and most advantageously from 60 to 85 per cent, of the active pore volume consist of pores of a diameter of between 0 and 2 $\mu\mu$; particularly good results are obtained if at least 15 per cent, preferably at least 25 per cent and most advantageously from 30 to 60 per cent, of the active pore

volume consist of pores of a diameter of between 0 and 1 $\mu\mu$.

It means already a great advantage if only the carrier mass of the catalyst, i. e. the skeleton left after dissolving out therefrom any additional catalytic materials satisfies the above conditions, but even better results are usually obtained if the finished catalyst, i. e. the carrier inclusive of the catalytic substance, satisfies the conditions. For brevity's sake the term "catalyst" is henceforth meant to cover both the finished catalyst and the carrier for the catalytic substance.

Investigations into the pore diameter of a material are preferably carried out by the Kubelka method (see "Kolloid Zeitschrift," vol. 55, 1931, page 129 et seq.) but a complete adsorption isotherm need not be made out. It rather suffices to ascertain the adsorption power of the porous mass towards benzene vapor from a hydrogen current at 13° or 20° C which at these temperatures possesses a relative saturation with benzene vapor of 1 per cent, 10 per cent and 90 per cent, respectively, which degrees of saturation, according to Kubelka's formula

$$D = \frac{B \cos \varphi}{-\log S}$$

(loc. cit., page 136 (5)) are known to correspond to pore diameters up to 1 $\mu\mu$, 2 $\mu\mu$ and 43 $\mu\mu$, respectively. In this formula D means the pore diameter in $\mu\mu$, S means the relative degree of saturation of the benzene vapor, B means a constant (1.87), and $\cos \varphi$ is equal to 1 for benzene according to Kubelka, (loc. cit., page 137, table XII).

The adsorption power for the different degrees of saturation is ascertained by determining (see Kubelka, loc. cit., pages 130/131) the increase in weight of the gel over which hydrogen with a relative saturation in benzene vapor of 1 per cent, 10 per cent and 90 per cent, respectively, is passed. The increase in weight is equal to the quantity of benzene adsorbed in the pores which, when divided by the specific gravity of benzene, indicates the pore volume corresponding to the above degrees of saturation.

The pore volume calculated from the adsorption power at a relative saturation of 90 per cent has been denoted herein as the "active pore volume," the "inactive pore volume" which exists in addition thereto and which only becomes obvious in the adsorption at a relative saturation of more than 90 per cent being ignored.

From among the numerous kinds of silica gels the fine-pored ones only come into considera-

tion; they are advantageously made according to the processes of the German Patents Nos. 574,721 and 626,272. In making the said gels it is of high importance first to prepare a weakly acid homogeneous sol, preferably one with a pH-value of between 2 and 5, preferably between 3 and 4.5, to form a jelly by allowing the sol to solidify and then, when washing the said jelly for a far-going removal of the salts formed during the sol-formation, to set up therein, a pH-value of between 2 and 6, more preferably between 3 and 5. On drying the pieces of jelly then shrink into solid granules of porous gel, the pore volume of which spreads over the said range of diameters in the ratio indicated.

Another procedure consists in setting up in the silica jelly or silica-alumina jelly, precipitated in the presence of an acid, a pH-value inferior to 2, preferably between 1 and 2, the drying by which the shrinking or formation of pores is to be accomplished, being carried not too far, but at the most to a content of water of from 20 to 40 per cent, removing part of the acid from the partially shrunk mass by a second washing until a pH-value of between 2 and 6, preferably between 3 and 5, has been set up, and then drying again. This method is the more preferred the more the pH-value is inferior to 2; for, if the water contained in the pure jelly or the jelly containing salts be completely replaced by concentrated sulphuric acid and the pole-formation be accomplished by complete shrinkage, fine-pored gels, which are suitable for use in the present process, would not result. The pH-value most suitable within the range of between 3 and 5 may be set up by removing acid from a jelly of stronger acidity or adding acid or acid media to a more weakly acid or neutral or only weakly alkaline jelly, preferably while this is being washed. The jelly consisting of silica gel or silica gel and some aluminum hydroxide or the waste jelly available in the form of small pieces may be shaped into cylinders or Raschig rings, preferably by means of an extrusion press, as described for instance in the German Patent No. 544,868, Example 1.

As a matter of course, the above directions not only apply to gels obtained by way of a sol, but also to precipitates and inhomogeneous jellies, in the manufacture of which an alkaline or extremely acid reaction are preferably avoided and a weakly acid reaction is maintained, provided these substances are brought to shrink at the said pH-value, preferably a pH-value of between 3 and 5. For the reason, however, that hard and coarse lumps are usually not obtained thereby, these precipitates or products obtained by drying the same must likewise be shaped in an extrusion or tableting press, preferably according to the methods disclosed in the U. S. Patents Nos. 1,751,955 and 1,832,153 or, after homogenization by a severe mechanical treatment, as disclosed in German Patents Nos. 557,337 and 542,321.

The pure gels, as also those which contain metal oxides, may be laden, for example with metal compounds, such as for example aluminum salts or colloidal solutions of alumina by subsequently treating them in known manner, for example by impregnation or, as described in the U. S. Patent No. 1,832,153, by shaping; suitable substances may also be incorporated in the mass already during the manufacture thereof, for example according to U. S. Patent No. 1,797,804 and German Patent No. 617,593. Among catalytic

additions to the silica sol or silica gel which, if desired, may contain alumina, we may mention above all the catalytic substances already known for the purposes in question, for example substances comprising metals from group 8 of the periodic system, in particular cobalt and iron, if desired, together with activating additions, such as thorium oxide, alkali metal salts, magnesia, additional alumina and the like.

The catalysts may be further improved by subjecting them to an after-treatment by thorough washing or acid treatment. An acid treatment, which according to its intensity results in a partial or complete removal of metal oxides, or other soluble substances contained in the mass or in a partial lading of the pores with small proportions of acid (sulphuric, hydrochloric, nitric or phosphoric acid), is followed equally by a thorough washing with distilled water and a drying, so that the final product is neutral or but extremely weakly acid.

For use as catalysts we may mention also synthetic bleaching earths or gels of the composition of synthetic bleaching earths or the thoroughly washed waste materials, so-called "Si-materials" containing hydrated silica and alumina and which result in the decomposition of minerals, earths, slags, or clays by means of acids, as for example sulphuric acid, hydrochloric acid, nitric acid or sulphurous acid, or the gels prepared therefrom, provided the pores of these materials have their diameters spread over the range of diameters above referred to.

The conversion of carbon monoxide with hydrogen to form hydrocarbons containing more than one carbon atom in the molecule, such as benzines, Diesel oils, lubricating oil and paraffin wax, in the presence of the said fine-pored catalysts is effected under the conditions of temperature and pressure customary for this conversion. Generally temperatures between about 150° and 450° C are employed according to the nature of the catalytically active metal. With catalysts comprising cobalt the temperatures are usually lower than with catalysts comprising iron. Ordinary or superatmospheric pressures, for example pressures of 2, 5, 10, 20, 50, 100, 200 or 500 or more atmospheres may be maintained. The gases may comprise equal parts of carbon monoxide and hydrogen or also an excess of carbon monoxide or of hydrogen. Also the other conditions are as usual.

The following Example serves to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said Example. The percentages and parts are by weight.

Example

100 grams of a fine-pored silica gel obtained by allowing a homogeneous sol (pH 3 to 4.5) to solidify, washing the jelly so obtained until a pH of between 3 and 5 has been reached and drying the jelly at from 200° to 300° C, the active pore volume of which gel consists of 35 per cent of pores with a diameter of between 0 and 1 μ of 35 per cent of pores with a diameter of between 1 and 2 μ and of 30 per cent of pores with a diameter of between 2 and 43 μ , i. e. of 70 per cent of pores with a diameter of between 0 and 2 μ , is saturated with water vapor, gradually soaked with a solution of 8 grams of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 50 cubic centimeters of water and dried at from 120° to 180° C.

100 parts by weight of the dried gel so obtained are heated for a short time to a temperature be-

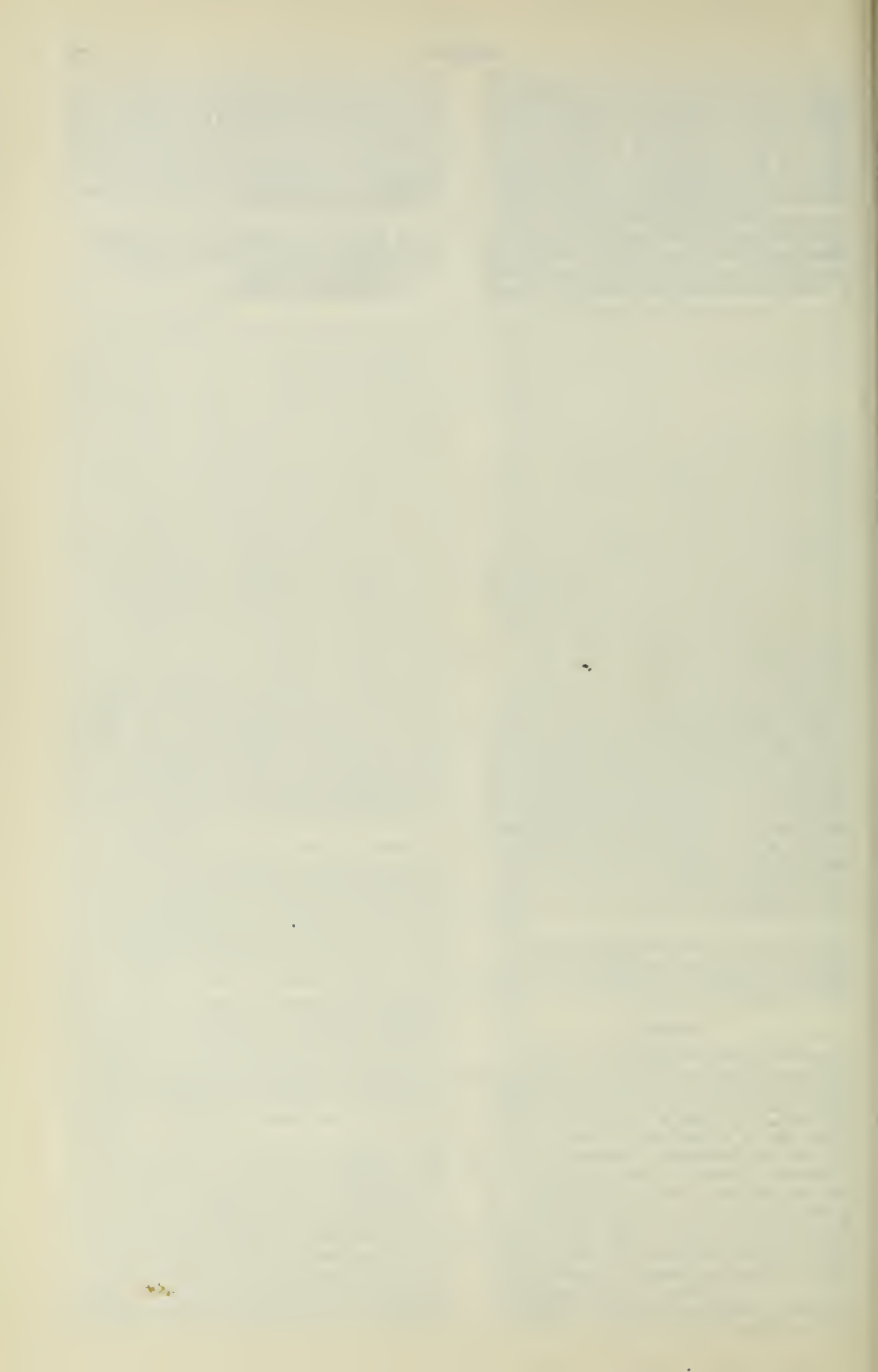
tween 700 and 1100° C and, after cooling, introduced into a solution of 200 parts by weight of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 2000 parts by weight of water. Thereupon the cobalt is precipitated on the silica gel by the addition of a solution of 175 parts by weight of potassium carbonate (K_2CO_3) in 2000 parts by weight of water. The solid mass is then separated from the solution, washed out and subsequently dried at 110° C.

When passing over the mass so obtained at a temperature of 194° C a gas mixture consisting of 1 part by volume of carbon monoxide and 2 parts by volume of hydrogen with a velocity of flow of

1.3 liters per each gram of cobalt and per hour liquid and solid hydrocarbons are obtained in a yield of 100 g per each cbm of initial gas.

If, however, a cobalt catalyst is employed which has been prepared from a silica gel having wide pores, only 70 g of liquid and solid hydrocarbons are obtained from each cbm of initial gas under otherwise the same conditions.

10 HEDWIG ELISABETH STOEWENER.
Administratrix of Fritz Stoewener, Deceased.
EMIL KEUNECKE.
FRIEDRICH BECKE.



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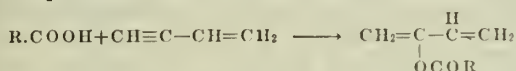
PROCESS OF FORMING ESTERS

Arthur Wolfram, Frankfurt am Main, and Hellmuth Jahn, Bad Soden (Taunus), Germany;
vested in the Alien Property Custodian

Application filed April 19, 1941

The present invention relates to a process of forming esters.

The addition of carboxylic acids $R.COOH$ to vinylacetylene in the liquid phase according to the equation:



with formation of the esters of 1,3-butadienol-2 is known. (U. S. A. Patent No. 1,963,108). Hitherto, however, only small yields have been obtained. Substantial portions of the esters resinify and compounds from 1 mol of monovinylacetylene and 2 mols of carboxylic acid are formed.

In the known processes there are used as catalysts for the reaction mercuric oxide or mercury salts, for instance, the sulfate or phosphate in combination with boron fluoride, sulfuric acid, SO_3 or sulfoacetic acid. The temperatures applied range from $0^\circ C$ to $+25^\circ C$, in some cases even up to $+60^\circ C$.

Now, we have found that the mercury salt of the carboxylic acid which just serves for carrying out the reaction is a very suitable catalyst without any adjuvant. For the addition of acetic acid mercury acetate is used, in the case of propionic acid mercury propionate is used and so forth. It is detrimental to add boron fluoride, sulfuric acid, SO_3 or the like in the quantities hitherto used since the ester formed is changed by these compounds.

The new catalysts become active only at temperatures above about $60^\circ C$, preferably at temperatures near $70^\circ C$ – $90^\circ C$. These high temperatures involve the danger of polymerization of the esters by heat. It has, however, been found furthermore that by addition of the usual stabilizing agents which prevent the polymerization such as thioldiphenylamine, methylene blue, dibenzyl- β -naphthylamine or the like the polymerization is prevented. The higher reaction temperature involves two important advantages for the preparation of the volatile esters: firstly, it is possible to perform the addition reaction continuously. This was not the case with the process hitherto known according to which the catalyst had to be destroyed before the ester obtained could be isolated. If higher temperatures are applied, however, arrangements may be made that the current of gas of the not yet reacted monovinylacetylene carries a mixture of carboxylic acid and ester away from the reaction zone. The mixture obtained which is entirely free from mercury salt consists, in case propionic acid is used, at a reaction temperature of $80^\circ C$ of 70–75 parts of pro-

pionic acid and 30–25 parts of ester. The mixture is removed, separated according to known methods, for instance, by distillation or extraction of one of the two components by means of a solvent, and the propionic acid is reconducted into the reaction zone. This method of working involves a second advantage, namely the non-formation of a by-product. In view of the fact that the ester formed is directly removed from the reaction zone, a product is no longer formed from 2 mols of carboxylic acid and 1 mol of monovinylacetylene.

It has, furthermore, been found that the degree of purity of the monovinylacetylene is of great importance. It is advantageous to carefully exclude the atmospheric oxygen, since it causes the catalyst to become quickly inactive. It is also advisable to exclude water.

The following acids are, for instance, suitable for preparing esters: acetic acid, propionic acid, butyric acid, isobutyric acid, n-heptylic acid, isoheptylic acid; furthermore, aromatic carboxylic acids such as benzoic acid and the homologues thereof, isocyclic carboxylic acids such as naphthenic acids. In case the melting point of an acid is too high, solvents which are indifferent against vinylacetylene may be applied, for instance, ethers, such as dibutylether, diisoamylether.

The following examples serve to illustrate the invention but they are not intended to limit it thereto, the parts being by weight:

(1) The apparatus as shown in the accompanying drawing is filled with nitrogen free from oxygen. Thereupon, 1000 parts of propionic acid and 350 parts of mercury propionate and 4 parts of thioldiphenylamine are heated to 80° in the reaction vessel R₁. The monovinylacetylene passes from the tank G through the gas meter U₁, through the gas purifier R₂ in which the gas is freed from the oxygen and through the drying device T into pump P which presses the gas into the reaction vessel R₁. During the passage of the monovinylacetylene the color of the mixture changes from green to violet. The current of gas carries a mixture of 70–75 parts of propionic acid and 30–25 parts of 1,3-butadienol-2-propionate into the cooler K in which the mixture is condensed and collects in the receiver V₂. From there the mixture of the liquids is distilled and the ester is freed from the propionic acid according to known methods. From the cooler K the gas current returns through the pump into the reaction vessel. Provision has been made to measure and draw off flue gas through the gas meter U₂. From the supply tank V₁ the propionic

acid is compensated in the reaction vessel R₁. The speed of circulation of the gas is chosen so that the gas is regenerated in the reaction vessel 80–100 times per hour. In the course of 116 hours 8250 parts of propionic acid are introduced. From the receiver V₂ 9968 parts of a mixture are removed which consists of 6810 parts of propionic acid, 2390 parts of 1,3-butadienol-2-propionate and 768 parts of dissolved monovinylacetylene. The operation is interrupted after 116 hours and the content of the column is examined. By cooling 167 parts of the compound mercury propionate+monovinylacetylene precipitate which are filtered with suction and used for a new batch. By distillation under reduced pressure a mixture of propionic acid and only 5% of ester is obtained. Higher-boiling by-products are not formed. Polymerizate is, likewise, not obtained. Metallic mercury is present only in traces. The residue, 268 grams, contains further addition product from mercury propionate+monovinylacetylene. The compound $\text{Hg}(\text{COC}_2\text{H}_5)_2 + x\text{C}_4\text{H}_6$ may be warmed in the dry state only with great care since it decomposes at higher temperatures while deflagrating.

The propionic acid may also be separated easily from the 1,3-butadienol-2-propionate by means of cold magnesium-chloride solution which dissolves the propionic acid and leaves the ester undissolved. From the solution the propionic acid may be obtained by treatment with organic solvents such as benzene whereupon it may again be caused to react with monovinylacetylene. This mode of working may also be applied for the reaction of other acids with monovinylacetylene.

(2) The addition of propionic acid to monovinylacetylene may also be performed discontinuously. In a flask provided with a stirrer 500 parts of propionic acid, 75 parts of mercury propionate and 2 parts of thioldiphenylamine are heated to 80° C and at this temperature monovinylacetylene is introduced during 50 hours. The operation is interrupted when the absorption decreases. The contents of the flask are cooled sharply whereby part of the catalyzer precipitates. The liquid is decanted and the dissolved monovinylacetylene is removed under pressure. There are obtained 643 parts which are distilled under reduced pressure. 466 parts thereof pass over between 35° C and 42° C under a pressure of 2 mm Hg. This fraction contains 222 parts of 1,3-butadienol-2-propionate and 244 parts of propionic acid. 28 parts of the mixture of esters pass over between 42° C and 83° C under a pressure of 2 mm Hg. 94 parts of the compound from 2 mols of propionic acid and 1 mol of monovinylacetylene follow between 99° C–102° C under a pressure of 2 mm. A remainder of 50 parts contains the residue of the mercury catalyzer.

(3) In the cyclic apparatus shown in the accompanying drawing there are heated to 75° C 1000 parts of acetic acid, 320 parts of mercury acetate and 4 parts of thioldiphenylamine. While passing monovinylacetylene therethrough, the color of the solution turns from green to violet. In the course of 50 hours 6460 parts of glacial acetic acid are introduced. During this time 8166 parts of a mixture are obtained which contains 1066 parts of 1,3-butadienol-2-acetate and 5880 parts of glacial acetic acid and about 1220 parts of dissolved monovinylacetylene.

(4) In a flask provided with a stirrer 1080 parts of glacial acetic acid are heated to 80° C together with 150 parts of mercury-acetate and 6 parts of thioldiphenylamine. Monovinylacetylene is introduced during 55 hours. The operation is interrupted when the absorption of the gas decreases. The contents of the flask are cooled. Part of the catalyzer crystallizes. The liquid is decanted and the monovinylacetylene is filtered with suction under reduced pressure. 1615 parts are distilled under reduced pressure. The first fraction passes over between 22° C–40° C under a pressure of 2 mm Hg. It amounts to 1122 parts and consists of 531 parts of 1,3-butadienol-2-acetate and 591 parts of acetic acid. The remainder in the flask amounts to 434 parts and contains the compound from 2 mols of acetic acid and 1 mol of monovinylacetylene, the residue of the mercury catalyzer and a small quantity of polymerizate.

(5) 440 parts of isobutyric acid and 86 parts of isobutyrate of mercury are heated at 80° C in a flask provided with a stirrer together with 2 parts of thioldiphenylamine. Monovinylacetylene is introduced for 32 hours. The operation is interrupted and the contents of the flask are cooled. Beautiful crystals of the mercury catalyzer precipitate which are removed. 577 parts are distilled under reduced pressure. Between 43° C and 60° C 444 parts pass over at 5 mm pressure Hg which consists of isobutyric acid and 1,3-butadienol-2-isobutyrate. Then follow between 90° C and 104° C under a pressure of 5 mm Hg 11 parts of an ester of higher boiling point, presumably the compound from 2 mols of isobutyric acid and 1 mol of monovinylacetylene. The remainder amounts to 64 parts and contains further ester of higher boiling point and the residue of the mercury catalyzer. The main fraction is introduced into ice water, neutralized by means of sodium carbonate, the oil is taken up in ether, dried over sodium sulfate and distilled under reduced pressure. Between 50° C and 54° C and under a pressure of 3–3.5 mm Hg pure 1,3-butadienol-2-isobutyrate distills. The yield amounts to 213 parts.

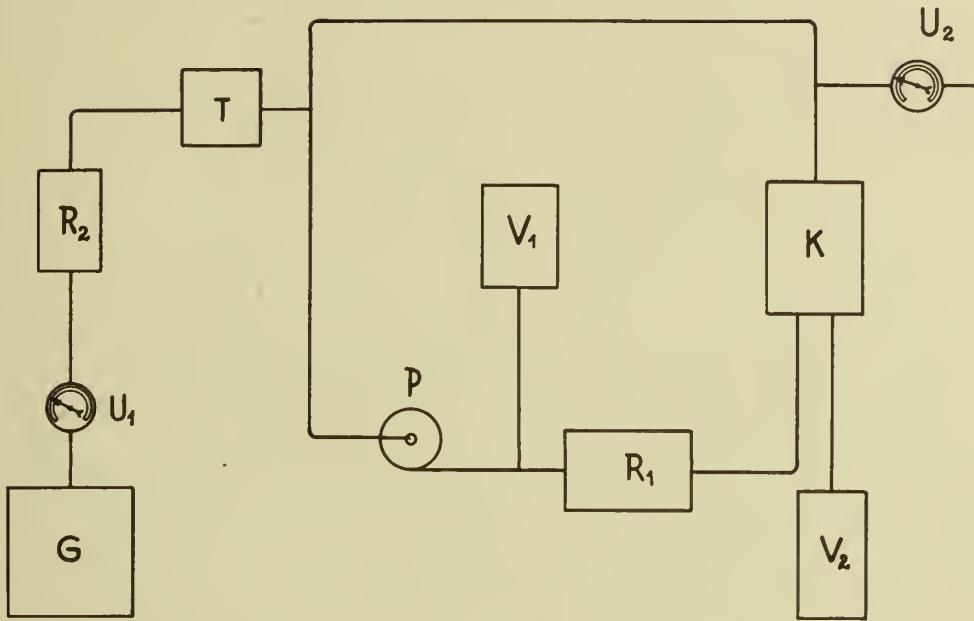
(6) 378 parts of isoheptylic acid and 105 parts of isoheptylate of mercury are heated together with 2 parts of thioldiphenylamine to 70° C in a flask provided with a stirrer. At this temperature monovinylacetylene is introduced in the course of 19 hours. The operation is interrupted and the mixture is allowed to cool. Part of the catalyzer separates in the form of a voluminous precipitate which is filtered with suction. 382 parts of liquid are distilled under reduced pressure. 320 parts pass between 90° C and 109° C under a pressure of 11–9 mm. The remaining 56 parts contain the residue of the mercury catalyzer. The fraction is introduced into water and neutralized by means of sodium carbonate while cooling with ice. The oil is separated, taken up in ether, dried over potassium carbonate and distilled after the ether has been driven off. Between 85° C and 92° C and under a pressure of 9 mm Hg the 1,3-butadienol-2-isoheptylate distills. The yield amounts to 67 grams.

ARTHUR WOLFRAM,
HELLMUTH JAHN.

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Arthur Wolfram
Hellmuth Jahn
INVENTORS

BY *Hubert Jahn*
THEIR ATTORNEYS

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HEAT-STABILIZED HIGH-POLYMER HALOGEN-CONTAINING PRODUCTS

Hans Fikentscher, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 19, 1941

The present invention relates to halogen-containing high-polymeric substances of improved heat stability.

High-polymeric substances containing halogen have marked tendency to split off hydrogen halide on heating. The hydrogen halide so liberated not only causes discoloration of the substances but also attacks the metallic parts of the equipments in which the substances are worked, for example rollers or molds, and also metallic parts embedded in the finished molded articles made from the high-polymeric substances.

It has already been proposed to add lead compounds as heat stabilizing agents. The poisonous effect of the lead compounds and their tendency to undergo discoloration in the presence of even slight quantities of hydrogen sulphide, however, prejudices their use in practice.

It is further well known to use basic substances, as for example alkali metal salts of weak organic acids, carbonates or hydroxides of the alkali metals or alkaline earth metals or organic nitrogenous compounds having a weak basic action, as heat stabilizing agents. These substances, indeed, absorb and neutralize the hydrogen halide split off in the heat, but on the other hand, on account of their alkaline reaction favour the splitting off of hydrogen halide from many high-polymeric substances containing halogen in the heat, so that in these cases completely colorless shaped articles cannot be obtained. Ureas and thioureas, too, have been proposed as stabilizing agents, but when admixed alone, they do not prevent the high-polymeric halogen-containing substances from becoming brown in the heat.

I have now found that the heat stability of halogen-containing high-polymeric substances is considerably improved by adding to them alkaline substances and in addition thereto amines or carbamides bearing a hydrogen atom replaceable by an alkali metal, as a stabilizing agent.

As alkaline substances may be mentioned, for example, the alkali metal and alkaline earth metal hydroxides and carbonates and salts of weak acids, especially organic acids or of boric acid, also basic phosphates.

Suitable amines or carbamides bearing at least one hydrogen atom replaceable by an alkali metal are, for example, diarylamines, as diphenylamine, furthermore thiourea and, in particular, arylthioureas, for example phenyl-, diphenyl-, dichlorodiphenyl-, ditolyl- and dinaphthylthioureas, furthermore arylureas and ureides.

Among high-polymeric halogen-containing substances which can be stabilized according to the present invention, may be mentioned, for example chlororubber, chlorinated butadiene rubber, polyvinyl chloride, chlorinated polyvinyl chloride, poly-as-dichlorethylene, polymeric chloracrylic compounds and interpolymerization prod-

ucts of the monomeric compounds forming the basis of the above polymerization products, either with one another or with other polymerizable substances. Also in the event of softeners being added to the polymerization products, the mixture of alkaline substances with the said amines or carbamides exerts its favorable stabilizing action.

The halogen-containing high-polymeric substances thus stabilized are well resistant even when heated for a long time. While the alkaline substances, indeed, will absorb and neutralize the hydrogen halide set free in the heat, their alkaline action appears to be lessened by the addition of an amine or carbamide of the said type.

The quantity of the alkaline substances and of the amines or carbamides may vary within rather wide limits. Generally speaking, additions of from 0.1 to 1 per cent. of an alkaline substance and of from 0.01 to 5 per cent. of an amine or carbamide of the said kind are most suitable. There is a definite rate and minimum of the stabilizing agents for each of the halogen-containing high-polymeric substances which brings about the best effect. This rate may easily be determined by experiments.

The stabilizing agents may be added in a dissolved, suspended or pulverulent state to the halogen-containing high-polymeric substances, which in their turn may be in a dissolved, dispersed or solid state. In practice, the stabilizing agents are advantageously incorporated with the halogen-containing high-polymeric substances as uniformly as possible distributed already before the substances are worked up in the heat, but they may also be added only when the substances are being worked in the heat, for example rolled or molded. The stabilizers may also be added during the preparation of the halogen-containing high-polymeric substances, for example during their polymerization.

On account of their improved heat stability the halogen-containing high-polymeric substances in accordance with the present invention they can be heat-molded forming completely colorless articles, whereas the shaped articles hitherto obtained in the heat were more or less discolored.

The following Examples serve to illustrate how the present invention may be carried out in practice but the invention is not restricted to the said Examples. The parts are by weight.

Example 1

Several batches of highly polymeric vinylchloride obtained by emulsion-polymerization are washed after precipitation from the emulsion with sodium carbonate solutions of various concentrations so as to incorporate each batch of the polymerization product with a definite percentage of sodium carbonate, as illustrated in the table below. The dried polymerization product is then

admixed with about 1 per cent of a wax as lubricant and with varying amounts of diphenylthiourea in a ball-mill. The samples withdrawn are rolled at 165° C for 15 minutes and finally stretched into sheets of 0.1 millimeters thickness. These sheets are then kept in a heat cabinet at 155° C for 2 hours. The discoloration of the sheets caused by this treatment is a measure of their heat-resisting quality. The sheets are inspected in an eightfold layer to better show the degree of discoloration.

The effect of the different percentages of the stabilizing agents on the heat-resistancy of the sheets will be seen from the data in the following table. This table in its columns d and e refers to ordinal numbers 1 to 9, which denote the depth of color as in the following list.

- 1=completely colorless
- 2=discoloration just visible
- 3=faintly light brown to light yellow
- 4=light brown
- 5=brown
- 6=strong brown
- 7=next to dark brown
- 8=dark brown
- 9=very dark brown.

In the table "clear" means that the sheets are distinguished by a striking clarity far superior to that of the other sheets.

Batch	Additions in per cent of—		Discoloration of the sheets after—	
	Sodium carbonate	Diphenyl thiourea	Rolling at 165° C for 15 min.	Storage for 2 hours (at 155° C)
	Per cent			
1.....	Less than 0.03	0	3-4	7
2.....	0.03	0.03	3-4	7-8
3.....	0.03	1.0	4	7-8
4.....	0.08	0.006	2	6-7
5.....	0.08	0.01	1	6-7
6.....	0.08	0.03	(1)1	6
7.....	0.08	0.15	(1)1	7
8.....	0.08	1.0	1	8
9.....	0.2	0	3	6
10.....	0.2	0.03	1-2	4
11.....	0.2	0.15	(1)1	2
12.....	0.2	1.0	1	2
13.....	0.4	0	3-4	5
14.....	0.4	0.03	1-2	5-6
15.....	0.4	0.15	1-1	3-4
16.....	0.4	1.0	1	1-2
17.....	0.4	3.0	1-2	2
18.....	0.4	5.0	1-2	2-3

¹ Clear.

² Yellowish.

As will be seen from the table the data given are for one addition alone and for two additions jointly. Where both substances are added their effect is not a mere aggregation of the individual effects, but the stabilizing effect of the sodium carbonate is considerably increased. Thus, for example, in batch No. 5 by the use of 0.08 per cent of sodium carbonate with an addition of 0.01 per cent of diphenylthiourea a far better effect is reached than in batch No. 3 where a hundred times larger amount of diphenylthiourea was used together with 0.03 per cent only of sodium carbonate. The table further shows that for every percentage of sodium carbonate the maximum effect and the best clarity is produced by a definite percentage of diphenylthiourea and that a larger addition will result in a distinct deterioration of the heat stability. Thus, for example, according to batch No. 6 the use of 0.08 per cent of sodium carbonate yields the best effect with an addition

of 0.03 per cent of diphenylthiourea which effect, as may be seen from batch No. 8, is diminished when adding 1 per cent of diphenylthiourea.

From the samples made up with 0.4 per cent of sodium carbonate (batches Nos. 13-18), No. 16 and 17 containing 1 and 3 per cent, respectively, of diphenylthiourea are apparently best in quality. The masses according to No. 16 which are practically not discolored even after a two hours' storage at 155° C, are especially suitable for making colorless molded articles which either during or after their manufacture are exposed to severe heating conditions.

The diphenylthiourea may be added in a pulverulent state or in solution, using methanol, for example, as a solvent, or in aqueous suspension. Thus, for example, the polyvinylchloride precipitated from the aqueous dispersion formed by the emulsion polymerization may be washed with a sodium carbonate solution saturated with diphenylthiourea. In this case, too, a colorless sheet is obtained after rolling at 165° C for more than 15 minutes. This latter method ensures a specially uniform distribution of the stabilizing agents, one or two passages through the roller being thus sufficient to obtain a beautiful and uniform sheet. Other arylated thioureas, as for example dinaphthyl-, ditolyl-, dichlordiphenyl- as well as phenylthiourea act similarly to diphenylthiourea. Phenylthiourea is readily soluble in water and therefore especially suitable for being added in an aqueous solution.

Similarly good results are obtained with interpolymerization products from vinylchloride and maleic esters or acrylic esters or with mixtures of these interpolymerization products with polyvinylchloride by an addition of 0.2 to 0.4 per cent of sodium carbonate and 0.15 to 1.0 per cent of diphenylthiourea.

Example 2

Several portions of polyvinylchloride as employed in Example 1 are washed with aqueous solutions of sodium carbonate and thiourea of varied concentrations so that the following percentages thereof are contained in the polyvinylchloride after drying. The masses are then rolled out into sheets according to Example 1 and tested as to their heat resistancy. The results of the tests are set out in the following table:

Batch	Additions in per cent. of—		Discoloration of the sheets after—	
	Sodium carbonate	Thiourea	After rolling at 165° C. for 15 min.	Storage for 2 hours at 155° C.
	Per cent			
1.....	Less than 0.03	0	4- 5	7
2.....	0.03	0.006	4-5	7-8
3.....	0.03	0.01	4	7-8
4.....	0.03	0.03	2-3	6-7
5.....	0.03	0.15	3	7
6.....	0.03	1.0	3-4	8
7.....	0.08	0	3	6
8.....	0.08	0.006	1-2	6
9.....	0.08	0.01	1	5
10.....	0.08	0.03	1-1	4
11.....	0.08	0.15	1-1	7
12.....	0.08	1.0	1	8
13.....	0.2	0.006	1-2	6
14.....	0.2	0.01	1	6
15.....	0.2	0.03	1-1	3
16.....	0.2	0.15	1-1	6-7
17.....	0.2	1.0	1	6-7
18.....	0.4	0.006	1	6
19.....	0.4	0.01	1	6
20.....	0.4	0.03	1	2
21.....	0.4	0.15	1-1	2
22.....	0.4	1.0	1-2	3

¹ Clear.

The comparison of this table with that given in Example 1 shows that thiourea imparts a similar initial stability as about four times its amount of diphenylthiourea, whereas the permanent stability achieved with thiourea is slightly inferior to that of diphenylthiourea.

Example 3

100 parts of polyvinylchloride as employed in Example 1 are made into a paste with a solution of 2.6 parts of a mixture of secondary and tertiary sodium phosphate and 300 parts of water. The paste thus prepared has a pH-value of 11. After removing the liquid by suction the polyvinylchloride is dried, mixed with 1 part of wax and 0.15 part of thiourea in a ball mill and then rolled out into a sheet at 165°C. The sheet

remains completely colorless even after rolling for more than 15 minutes, whereas a sheet to which no thiourea was added, has assumed a red-brown color in the same time. A similarly good result is obtained by adding 0.5 part of diphenylthiourea instead of thiourea.

Example 4

100 parts of polyvinylchloride as employed in Example 1 is mixed with 1 part of sodium stearate and 1 part of diphenylthiourea and rolled out into a sheet at 165° C. The sheet obtained is practically colorless and, even after continued heating at 155°C, becomes less brown than an equal sheet without an addition of diphenylthiourea after 15 minutes' rolling.

HANS FIKENTSCHER.

ALIEN PROPERTY CUSTODIAN

PROCESS OF PREPARING N-MONOCHLORINATION PRODUCTS OF HIGH-MOLECULAR FATTY ACID AMIDES

Ludwig Orthner, Frankfurt am Main, and Theodor Jacobs, Weisbaden, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 19, 1941

The present invention relates to a process of preparing N-monochlorination products of high-molecular fatty acid amides useful as intermediate products in the manufacture of auxiliaries in the textile industry.

N-chlorinated products of carboxylic acid amides are formed as intermediate products in the reaction of carboxylic acid amides with chlorine in the presence of alkali to obtain primary amines. This Hoffmann reaction can be carried through with success only with carboxylic acid amides of low molecular weight; it fails when compounds having more than 8 carbon atoms are used. It is already known by "Bericht der Deutschen Chemischen Gesellschaft," 30, 1897, page 899 to prepare palmitic acid chloramide by the action of a large excess of hypochlorous acid and sodium hypochlorite on a saturated alcoholic solution of palmitic acid amide. This method is regarded as very complicated and troublesome and, as has been found, cannot be carried through in a satisfactory manner.

Now we have found that N-chlorination products of high molecular fatty acid amides are readily obtained at ordinary temperature or a slightly raised temperature by causing chlorine to act upon aqueous suspensions of fatty acid amides having at least 16 carbon atoms. Care must suitably be taken for using the acid amides in as fine a subdivision as possible. The finer the subdivision, the purer are the chlorinated products obtained. A particularly fine suspension may be obtained by a small addition of the usual water-soluble distributing agents, for instance the alkylated or aralkylated naphthalene-sulfonic acids, the sulfonates of fat, alcohols, the reaction products of oleic acid chloride and methyl-taurine, the condensation products of ethylene oxide and hydroxyl compounds of high molecular weight. Useful suspensions are likewise obtained by other methods, for instance by dissolving the acid amide in acetone and pouring the solution obtained into water or dilute acetic acid. Fatty acid chloro-amides in a pure, readily filterable form are obtained in a technically simple manner and a theoretical yield according to the process herein described. The products obtained may be used as intermediate products for the manufacture of adjuvants in the textile industry.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight:

(1.) 28.3 parts of ground, commercial stearic acid amide melting at 98° C. are treated in a ball mill together with 50 parts of water and 0.3 part

of a paste of oleic acid methyl tauride of 35 per cent strength until after several hours a fine magma is obtained which is introduced together with 150 parts of water into a chlorination vessel having a capacity of 500 cc. and being provided with a stirrer. At about 30° C. a moderately rapid current of chlorine gas is then introduced in a quantity somewhat above the theoretical quantity. 100 cc. of 30° C. are again added and such a further quantity of chlorine gas is introduced as is necessary for rendering visible crystalline products in the reaction mass which is at first of a milky and turbid appearance. The crystalline products generally become visible in the presence of an excess of chlorine of 10 to 15 per cent. The whole is allowed to cool and stirring is continued for some hours at ordinary temperature.

The mono-chlorination product is filtered with suction, carefully washed and well pressed. The yield amounts to 100 per cent. Stearic acid monochloroamide is soluble in ether to a clear solution and melts at 67° C. to 68° C. Bodies having a melting point substantially higher than that afore-named indicate an incomplete chlorination and bodies of a melting point considerably below 67° C.-68° C. give a hint at a per-chlorination.

The stearic acid mono-chloroamide is stable but not for any length of time. The initially odorless substance gives off after a prolonged standing—and still more rapidly on drying—considerable portions of chlorine already at a moderate temperature under reduced pressure; the body gradually becomes more sparingly soluble in ether and assumes a higher melting point by the re-formation of stearic acid amide.

Analysis of a test dried on clay:

Found 11.25 per cent of Cl calculated 11.18 per cent

Found 4.7 per cent of N calculated 4.4 per cent.

If palmitic acid amide is treated in an analogous manner there is obtained palmitic acid monochloroamide melting at 69° C.-70° C. when dried on clay.

Analysis

Found 12.8 per cent of Cl calculated 12.2 per cent

Found 4.53 per cent of N calculated 4.6 per cent.

The chemical behavior of the compound very much resembles that of the stearic acid monochloroamide.

(2.) 28.3 parts of commercial stearic acid amide are dissolved on the vapor bath in 60 cc. of glacial

acetic acid. The solution is slowly poured, while rapidly stirring, into a mixture of 250 cc. of water and 100 cc. of acetone and the whole is stirred for some time. The theoretical portion of chlorine is then introduced at 30° C.-35° C. Towards the end of the chlorination process the mixture which is at first milky and turbid becomes transparent and the chlorine compound separates in crystal lumps. The whole is further stirred for 1-2 hours and diluted with water. The product

is filtered with suction and washed with water. This method of operating has the advantage that the grinding of the starting substance may be avoided and that only the substantially theoretical quantity of chlorine is required. The termination of the process is evident by the fact that the supernatant liquid becomes entirely clear so that a perchlorination is not possible.

LUDWIG ORTHNER.
THEODOR JACOBS.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF OXIMES

Friedrich Laucht, Leuna, Germany; vested in the Alien Property Custodian

Application filed April 24, 1941

The present invention relates to a process for the production of oximes.

I have found that the oximes of cyclohexanones (including cyclohexanone itself, its homologues and mixtures thereof) can be prepared in an advantageous manner by starting, instead of from pure cyclohexanones, from their mixtures with cyclohexanols, such as are obtained in the production of cyclohexanones by catalytic dehydrogenation of cyclohexanols. According to my invention the cyclohexanones are converted into oximes while in admixture with the cyclohexanols and the major portion of the oximes which separates out in a solid state is removed, for example by filtration or centrifuging, whereupon the residual liquid is subjected to a rectifying distillation with steam. This distillation yields first runnings of any cyclohexenes if such are present at all; then, contrary to expectation, the total amount of the cyclohexanols containing but slight proportions of oximes distills over; the proportion of oximes contained in the cyclohexanols, varies depending on the distillation conditions between about 1 and 6 per cent only of the total quantity of oximes. These cyclohexanol-cyclohexanone oxime mixtures obtained by the distillation with steam are preferably worked up by reconverting the oximes into cyclohexanones by treatment with an excess of acid, distilling the mixture of cyclohexanols and cyclohexanones obtained (advantageously by means of steam) and subjecting it to dehydrogenation in order to convert the cyclohexanols into cyclohexanones, which then are again converted into oximes and so on.

The distillate obtained by subjecting such mixtures of oximes and cyclohexanols subsequently to their treatment with an acid to a distillation with steam (as described above) contains, in addition to the cyclohexanols, only about half the calculated amount of cyclohexanones. A solution of oximes and hydroxylamine salts remains behind as the residue of this steam distillation, from which the oximes may be set free by the addition of alkali. The said solution of the salt containing oxime and hydroxylamine can also be added directly to a fresh portion of the initial mixture of cyclohexanones and cyclohexanols to be converted into oximes and so directly returned to the process. It is advantageous that the treatment with an excess of acid yields a larger proportion of oxime salt, because this can be directly returned to the stage in which the oxime is formed. In this manner, all

of the substances employed for the reaction are completely utilized.

The use of crude cyclohexanones containing cyclohexanols offers considerable advantages. Cyclohexanones, as is known, are prepared by the catalytic dehydrogenation of cyclohexanols in the vapor phase, in which treatment part of the cyclohexanols, usually from about 10 to 20 per cent, remains unchanged. The separation of these unchanged cyclohexanols, however, is difficult and expensive to perform, since the cyclohexanones, which are by far preponderant in quantity to the cyclohexanols, must be distilled off from the latter. With mixtures of homologues the separation of the single components and also a sharp separation of the total quantity of the cyclohexanols from the cyclohexanones, is altogether impossible or hardly possible for the reason that the boiling points of the components of such mixtures overlap, as appears from the following table:

Substance	Boiling point °C
Cyclohexanone	155
2-methylcyclohexanone	165
3-methylcyclohexanone	169
4-methylcyclohexanone	171
Dimethylcyclohexanones	170-182
Cyclohexanol	160
2-methylcyclohexanols	166-169
3-methylcyclohexanols	171-174
4-methylcyclohexanols	173-175
Dimethylcyclohexanols	179-189

From such mixtures cyclohexanone can be distilled off in a purity of about 98 per cent only. If such product is used for the conversion into oxime by the usual method a loss of cyclohexanol occurs. The process in accordance with the present invention, in contrast thereto, allows to produce pure oximes without the occurrence of losses in cyclohexanones or cyclohexanols. It is surprising that the cyclohexanols can be separated smoothly and with no danger whatever from the oximation mixture by steam distillation, since the ordinary distillation of a mixture of cyclohexanonoximes and cyclohexanols presents the serious danger of a decomposition and explosion, even when being carried out under reduced pressure. Moreover, it was to be expected that the cyclohexanonoximes would be reconverted by steam into the cyclohexanones. As a matter of fact such a reconversion does not occur.

The following Example will further illustrate with reference to the accompanying diagram-

matic drawing how the invention may be carried out in practice but the invention is not restricted to this Example.

Example

Cyclohexanol is delivered through line 1 to a vessel 2 in which it is dehydrogenated in known manner with the aid of catalysts at an elevated temperature. The product so obtained which consists, for example, of 84.5 per cent of cyclohexanone, 15 per cent of cyclohexanol and 0.5 per cent of cyclohexene, is passed through line 3 into the stirring vessel 4; a mixture of the calculated quantity of hydroxylamine sulphate with twice its quantity of water is supplied to the said vessel 4 through line 5. The reaction mixture is vigorously stirred and cooled, while introducing through line 6 sufficient gaseous ammonia to neutralize the sulphuric acid liberated during the reaction.

The reaction mixture is conveyed through line 7 to the centrifuge 8 where pure cyclohexanonoxime is separated in an amount of about 87 per cent (with reference to cyclohexanone contained in the mixture employed). The liquid freed from solid oxime consists of an aqueous solution of ammonium sulphate and a solution of cyclohexanonoxime which has not separated out and cyclohexene in cyclohexanol; it is passed through line 9 into a still provided with the distilling column 10 where it is subjected to a rectifying distillation with steam generated from water supplied through line 11. During this distillation an azeotropic mixture of a little water and the cyclohexene is taken out at the top of the column through line 12 at a temperature of about 70°C. Through line 13 a mixture of about 80 per cent of cyclohexanol and about 20 per cent of cyclohexanonoxime together with steam distills into the separator 14 where the water

separates as a layer; it is conveyed through line 11 to the still of the distilling column 10. The upper layer passes through line 15 into the still of the distilling column 16. Through line 17 an excess of sulphuric acid of 10 per cent strength is introduced; water is supplied through line 18 and evaporated in the still of column 16. The distillate from this steam-distillation flows through line 19 into the separator 20 where the water separates as a bottom layer from the mixture consisting of about 90 per cent of cyclohexanol and about 10 per cent of cyclohexanone. The water is returned to the still of column 16 through line 18 and the mixture of cyclohexanol and cyclohexanone passed back to the dehydrogenation vessel 2 through line 21.

The residue remaining in the still of the distilling column 10, consisting of cyclohexanonoxime and an aqueous solution of ammonium sulphate, passes through line 22 into the centrifuge 23 where the oxime is separated off. Its amount corresponds to about 10 per cent of the cyclohexanone employed. The solution of ammonium sulphate is led off through line 24 to the vessel 25 where it is evaporated to dryness. The sulphate may be used for fertilizing purposes. The steam generated during the evaporation may be passed to the stills of the distilling columns 10 and 16 through lines 26 or 27 and 18, respectively, if so desired.

The distillation residue remaining in the still of column 16 consists of an aqueous solution of cyclohexanonoxime sulphate and hydroxylamine sulphate. This mixture is led back through lines 28 and 5 to the stirring vessel 4 or the oxime is set free by means of alkali and recovered by filtration or centrifuging.

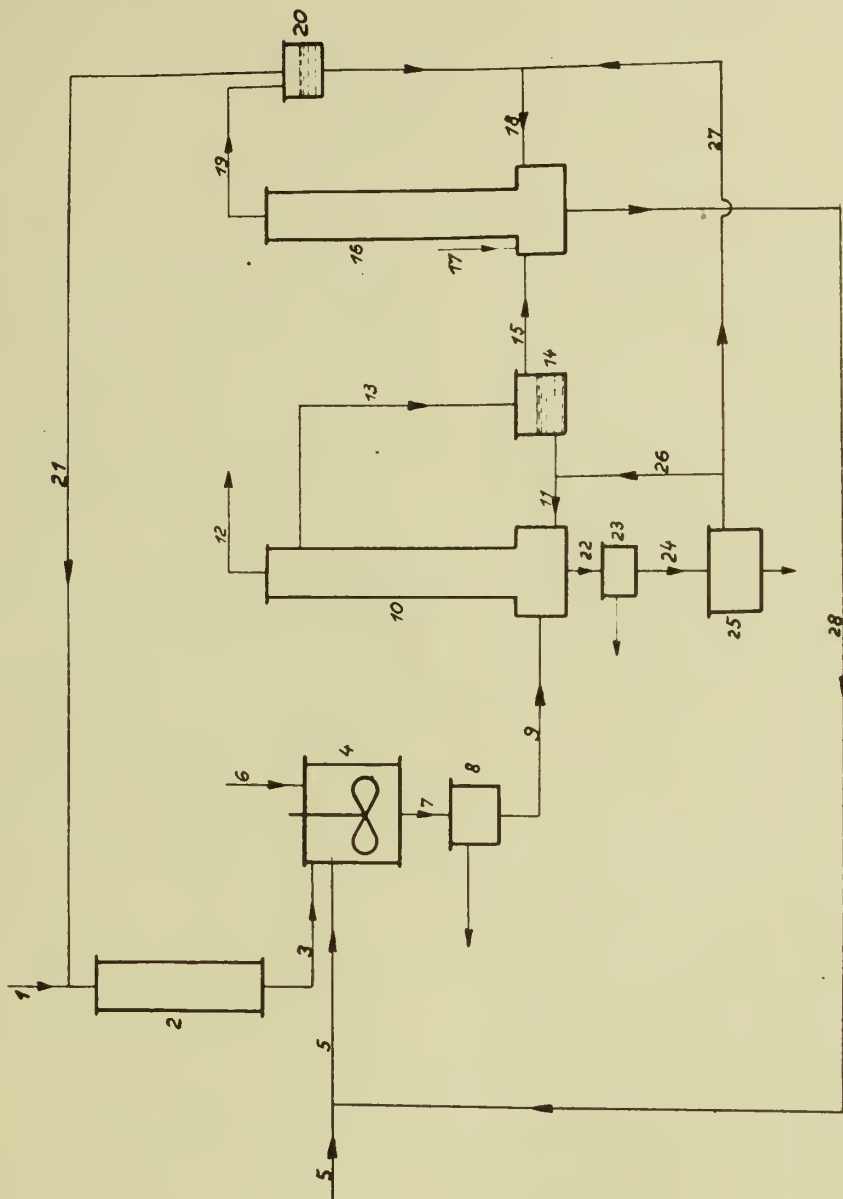
FRIEDRICH LAUCHT.

APRIL 20, 1943.

PROCESS FOR THE PRODUCTION OF OXIMES

BY A. P. C.

Filed April 24, 1941



INVENTOR.
BY *Friedrich Lanchet*
Hutz and Joslin
his ATTORNEYS

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREPARATION OF VITAMIN B₁ AND OF SIMILARLY BUILT COMPOUNDS

Rezső König, Árpád Gerecs and Zoltán Földi, Budapest, Hungary; vested in the Alien Property Custodian

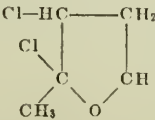
No Drawing. Application filed April 24, 1941

The present invention relates to a new process for preparing Vitamin B₁ and similarly built compounds. This process consists in subjecting a member of the group consisting of γ -aceto- γ -halogene-propyl alcohol [its cyclic form, ethers of the cyclic form, semi-cyclic form of γ -aceto- γ -halogene-propyl alcohol] to the action of reagents generally used for substituting an alcoholic hydroxyl group with a halogene atom and in subjecting the 2-methyl-2,3-dihalogene-tetrahydrofurane, thus obtained, to the action of 2-alkyl-4-amino-5-[thioformamido-alkyl]-pyrimidines.

A preferred form of the invention consists in subjecting a member of the group consisting of γ -aceto- γ -chloro-propyl alcohol [its cyclic form, ethers of the cyclic form, semi-cyclic form of the γ -aceto- γ -chloro-propyl alcohol] to the action of reagents generally used for substituting a hydroxyl group with chlor atom and in subjecting the 2-methyl-2,3-dichloro-tetrahydrofurane, thus obtained, to the action of 2-methyl-4-amino-5-[thioformamido-methyl]pyrimidine. One may further proceed in subjecting reaction mixtures containing one or more member of the group consisting of γ -aceto- γ -chloro-propyl alcohol, its cyclic form, its semi-cyclic form, an ether of the cyclic form of the γ -aceto- γ -chloro-propyl alcohol, to the action of hydrochloric acid and in subjecting the 2-methyl-2,3-dichloro-tetrahydrofurane, thus obtained, to the action of 2-methyl-4-amino-5-[thioformamido-alkyl]-pyrimidine.

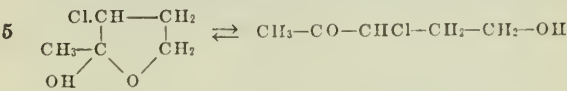
The action of the 2-methyl-2,3-dihalogene-tetrahydrofurane on 2-alkyl-4-amino-5-[thioformamido-alkyl]-pyrimidine is preferably carried out in formic acid as reaction medium. One may use preferably an acid binding agent, such as tertiary bases [pyridine], or alkali salts of organic acids [e. g. potassium formate or sodium benzoate] which will bound the haloic acid, such as hydrochloric acid, formed during the reaction.

Another object of the present invention is to provide for methods to prepare 2-methyl-2,3-dichloro-tetrahydrofurane, which have been unknown till now. For this purpose one may subject γ -aceto- γ -chloro-propyl alcohol to the action of gaseous hydrogen chloride while the following compound is formed:

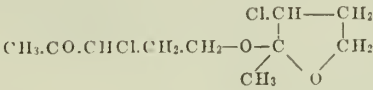


The γ -aceto- γ -chloro-propyl alcohol exists main-

ly—as described in the literature—in the cyclic form, this form being in a relation of desmotropy with the open chain form:



Thus, the so-called aceto-chlor-propyl alcohol is a mixture of the two desmotropic forms. The γ -aceto- γ -chloro-propyl alcohol prepared as described in several previous papers [such as Buchman Jour. of Americ. Chem. Soc. 58, 1083-84, Todd and Bergel, Journ. of the Chem. Soc., London 1937, 364-67 and Stevens and Stein loc. cit.] contains more or less considerable amounts of a semi-cyclic form that is of an ether which is built up from the cyclic form and from the open chain form, which ether has the following formula:



as shown by Stevens and Stein in the Journ. of the Americ. Chem. Soc., vol. 62, page 1045. All these parent components of the γ -aceto- γ -chloro-propyl alcohol are apt to the same reaction with reagents generally used for substituting a hydroxyl group with a halogene group. Therefore, all γ -aceto- γ -chloro-propyl alcohols obtained by the different prescriptions to be found in the literature can be used as starting materials with the same good result and it is not necessary to separate the different parent constituents from each other. In the following, when γ -aceto- γ -chloro-propyl alcohol is mentioned without further designation, the chemically pure γ -aceto- γ -chloro-propyl alcohol itself, or the γ -aceto- γ -chloro-propyl alcohol in a quality as described by Todds and Bergel [loc. cit.], or as described by Buchmann [loc. cit.], or as described by Stevens and Stein [loc. cit.], or mixtures thereof are to be meant. The experiments described have been effected with the same good results with the different types enumerated above.

The 2-methyl-2,3-dichloro-tetrahydrofurane can be prepared also by decarboxylating the aceto-chloro-butylolactone with concentrated hydrochloric acid, saturating the reaction mixture with hydrogen chloride gas and removing the formed tetrahydrofurane-dichloro derivative. This dichloride can also be obtained by other methods, e. g. by subjecting aceto-chloro-propyl alcohol to the action of thionylchloride. The de-

tails of the preparation of the abovementioned product can be found in the following.

One proceeds by starting from aceto-chloro-propyl alcohol as follows:

50 g of aceto-chloro-propyl alcohol are saturated while cooling in a frigorific mixture with dry hydrogen chloride gas. One observes about 18 g of increase of weight and an aqueous layer separates. Dehydrated sodium sulfate is added to the reaction mixture; then the obtained oil is decanted and distilled in vacuo under a pressure of 2 mm Hg. At about 45° 47–50 g of 2-methyl-2,3-dichloro-tetrahydrofuran are obtained. The product distills by atmospheric pressure in part under decomposition, or:

5 g of the alcohol are poured over with 5 g of thionyl-chloride. One observes a raising of temperature and development of gas. The mixture is kept then for 1 hour at 50° and the excess of thionylchloride is distilled off in the vacuo of a blast-pump. The residual oil is distilled in vacuo at a pressure of 0.5 mm Hg. At the temperature of about 39–43° 2.8 g of 2-methyl-2,3-dichloro-tetrahydrofuran distills, which forms a colourless mobil liquid a little fuming on the air. It contains about 43.5% of chlor.

It can be prepared from aceto-chloro-butyrolactone in the following manner:

50 g of aceto-chloro-butyrolactone and 25 ccm of concentrated hydrochloric acid are stirred for 3 hours at 35°. During this the formation of carbonic acid stops. By heating the mixture to 50° no remarkable formation of carbonic acid can be observed. Afterwards the mixture is cooled with a frigorific mixture and saturated during three hours with hydrogen chloride gas. The obtained oil is taken up in chloroforme dried with dehydrated sodium sulfate, then the chloroforme is removed and the residual oil is fractionated in vacuo at a pressure of 1 mm Hg. One obtains 26–28 g of 2-methyl-2,3-dichloro-tetrahydrofuran containing about 45% of chlor.

The product can be obtained starting from aceto-chloro-butyrolactone also in the following manner:

It is mixed with about 1 mol. of water and is saturated at room temperature under stirring with hydrogen chloride gas. It is stirred until no formation of carbonic acid is observed. In the meantime the temperature can be raised to 35–40°. Afterwards it is cooled in a frigorific mixture, saturated with hydrogen chloride gas and shaken out with petrolether. After the removal of the petrolether the residual product is fractionated. The fraction distilling at about 50° in vacuo at a pressure of 8 mm Hg contains the 2-methyl-2,3-dichloro-tetrahydrofuran.

One may proceed starting from aceto-chloro-butyrolactone also as follows:

50 g of aceto-chloro-butyrolactone and 6 ccm of hydrochloric acid of 5 volumetric percentage are stirred for few hours on the water bath until the end of the formation of carbonic acid. One observes the theoretical loss of weight; at the same time the two original layers also disappear. Afterwards the reaction mixture is cooled in a

frigorific mixture and saturated with hydrogen chloride gas. The formed oil is taken up in chloroforme, or rather in petrolether, then the solution is dried eventually with dehydrated sodium sulfate and after removing the solvent the residual oil is fractionated at a pressure of 1 mm Hg. One obtains about 35 g 2-methyl-2,3-dichloro-tetrahydrofuran containing about 44–45% of chlor.

Details for the preparation of Vitamin B₁ or of similarly built compounds are to be found in the following with the remark that instead of the latter mentioned pyrimidine compound also homologous compounds can be used.

To 10 ccm of formic acid of 91% first 7.7 g of 2-methyl-2,3-dichloro-tetrahydrofuran, then under cooling in icewater 3.9 g of pyridine are added. To this mixture 5 g of 2-methyl-4-amino-5-[thioformamido-methyl]-pyrimidine are added. The temperature raises slightly and a crystalline compound precipitates, then the reaction mixture is kept for 40 hours in an incubator of 50°. One obtains a light brown solution to which 45 ccm of abs. alcohol and 5 ccm of abs. alcohol containing 30% of hydrogen chloride gas are added. After boiling the mixture, the Vitamin B₁ crystallizes in form of white crystal plates. The mixture is kept for 1–2 hours in ice-water, filtered by suction and washed with 20 ccm of abs. alcohol. The product dried in vacuo weighs 4.5–5.3 g and melts at about 240°.

In the foregoing example the pyridine was used as acid binding agent. In the following example the use of potassium formiate is shown:

Under cooling and stirring to 2 ccm of formic acid of about 100% 1.5 g of 2-methyl-2,3-dichloro-tetrahydrofuran, 0.85 g of dry potassium formiate in form of a fine powder and 1 g of 2-methyl-4-amino-5-[thioformamido-methyl]-pyrimidine are added, then the reaction mixture thus obtained is kept for 65 hours in an incubator of 50°. Afterwards 9 ccm of abs. alcohol and 1 ccm of abs. alcohol containing 30% of hydrogen chloride gas are added to the reaction mixture which is then boiled. The crystals precipitating at cooling are filtered by suction after about an hour standing. The crystals are dissolved in water and 20 ccm of a hot aqueous solution of 1.7 g ammonium picrate are added. The obtained picrate is filtered, after a short standing, by suction, washed with water and dried in vacuo. One obtains about 2.3 g of picrate having a melting point of 203–204°. Then, the picrate is boiled in 20 ccm of abs. alcohol, then 5 ccm of abs. alcohol containing 30% of hydrogen chloride gas are added while the picrate goes, temporary, into solution. Then the hydrochloride of the Vitamin B₁ crystallizes. After standing for an hour the Vitamin B₁ crystals are filtered by suction, washed with 10 ccm of abs. alcohol and dried in vacuo. One obtains about 0.9 g of Vitamin B₁ melting at 248°.

REZSÖ KÖNIG.
ÁRPÁD GERECES.
ZOLTÁN FÖLDI.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREPARATION OF VITAMINS OF THE TYPE B₁

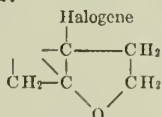
Rezső König, Árpád Gerecs and Zoltán Földi,
Budapest, Hungary; vested in the Alien Property Custodian

No Drawing. Application filed April 28, 1941

The present invention relates to a new useful process for the preparation of Vitamin B₁ and of similarly built compounds. This process consists in subjecting 2-methyl-2,3-dihalogene-tetrahydrofuranes to the action of reagents generally used for splitting off haloic acids and in subjecting the product, thus obtained, i. e. the unsaturated—with the elements of 1 mol. water poorer—derivative of 2-methyl-2-oxy-3-halogene-tetrahydrofurane to the action of 2-alkyl-4-amino-5-(thioformamido-alkyl)-pyrimidine.

An advantageous form of this process consists in subjecting 2-methyl-2,3-dichloro-tetrahydrofurane to the action of reagents generally used for splitting off hydrochloric acid and in subjecting the product, thus obtained, i. e. the unsaturated—with the elements of 1 mol. water poorer—derivative of 2-methyl-2-oxy-3-chloro-tetrahydrofurane to the action of 2-methyl-4-amino-5-(thioformamido-methyl)-pyrimidine.

The unsaturated—with the elements of 1 mol. water poorer—derivatives of the 2-methyl-2-oxy-3-halogene-tetrahydrofurane, which are intermediary products in the present process, have the following formula:



in which two vicinals of the three free valences form a double bound while the third free valence is saturated with hydrogen, to the action of 2-methyl-4-amino-5-(thioformamido-methyl) pyrimidine.

These products can be obtained, as already mentioned, by splitting off haloic acid from the 2-methyl-2,3-dihalogene-tetrahydrofurane, such as 2-methyl-2,3-dichloro-tetrahydrofurane, or directly from aceto-chloro-propyl alcohol as well by the action of phosphorous halogenides, such as phosphorous oxychloride, or phosphorous trichloride and by treating the reaction mixture with agents, such as pyridine, capable of splitting off haloic acid.

The preparation of 2-methyl-2,3-dihalogene-compounds is described in details in our co-pending patent application Ser. No. 390,124, filed April 24, 1941. Therefore, we describe in the following the preparation of the starting materials only in brief outlines. So e. g. 50 g of aceto-chloro-propyl alcohol or its ether described by Stevens and Stein (Journ. Amer. Chem. Soc., 1940, page 1046), which boils in vacuo of 1 mm Hg pressure at 111-112°C, are saturated undercooling in a

frigorific mixture with hydrogen chloride gas, then anhydrous sodium sulphate is added to the reaction mixture, the oil is decanted and distilled in a vacuo of 2 mm Hg. At about 45° about 50 g of 2-methyl-2,3-dichloro-tetrahydrofurane distille. Out of this product the unsaturated—with the elements of 1 mol. water poorer—derivative of 2-methyl-2-oxy-3-chloro-tetrahydrofurane can be obtained in the following manner:

To 15 g of 2-methyl-2,3-dichloro-tetrahydrofurane the calculated amount of dry pyridine is added, whereupon a white crystalline mass of salt is formed, which is heated for about ½ hour (at an inside temperature of about 110-130° C). Two layers separate. After cooling the upper layer is decanted, or separated in another way. The oil is distilled at a pressure of 50 mm Hg. At about 50° 7-8 g of the unsaturated—with the elements of 1 mol. water poorer—derivative of 2-methyl-2-oxy-3-chloro-tetrahydrofurane are obtained.

The splitting off the haloic acid can also be preferably effected by salts of organic acids:

15.5 g of 2-methyl-2,3-dichloro-tetrahydrofurane and 14.4 g of dry sodium benzoate are mixed. A development of heat can be observed. The mixture is stirred while cooling. When the sodium benzoate has gone into solution the mixture is kept for an hour in a water bath of about 60° C. Then the reaction mixture is distilled at a pressure of about 50 mm Hg in an oil bath. The recipient is kept in a frigorific mixture. During the distillation the temperature of the oil bath is slowly elevated until 120° C is reached. The distillation weighs about 10.2 g and distilles at about 40 mm Hg pressure at about 49-50° C. The chlor content of the product is 29.8%.

The unsaturated furane derivative can also be prepared from dihalogene furane derivatives, obtained in another way. For instance one may transform acetochloro-propyl alcohol with thionylchloride into 2,3-dichloro-furane derivative and split off from this hydrogen chloride. But one may also proceed by mixing, under cooling, 3 mol. of aceto-chloro-propyl alcohol with cca 1-1.5 mol. of phosphorous oxychloride or phosphorous trichloride (preferably in chloroforme as medium), then by adding a quantity of pyridine equivalent to the chlor content of the phosphorous halogenide and by heating the reaction mixture. The chloroforme is distilled off and the unsaturated—with the elements of 1 mol. water poorer—derivative of 2-methyl-2-oxy-3-chloro-tetrahydrofurane is separated from the residue either directly by distillation or by extracting with a solvent.

Details of the preparation of Vitamin B₁ or of similarly built compounds can be found in the following:

10 g of 2-methyl-4-amino-5-(thioformamido-methyl)-pyrimidine, 14 g of the unsaturated—
with the elements of 1 mol. water poorer—deriva- 5
tive of 2-methyl-2-oxy-3-chloro-tetrahydrofu-
rane and 10 ccm formic acid of about 91% are
heated for 40 hours at 50° in an incubator. Then
100 ccm of abs. alcohol and 10 ccm of abs. alco- 10
hol containing 30% of hydrogen chloride gas
are added to the light brown reaction mixture.
After standing for some hours 9–10 g of Vitamin
B₁ crystallize in form of white crystalline powder.

It melts at about 243–245°. Its content of chlor
is 20%.

One proceeds in the same manner when start-
ing from the corresponding bromo-tetrahydro-
furane derivative condensing this with 2-methyl-
4-amino-5-(thioformamido - methyl) -pyrimidine
or by starting from the chloro-tetrahydrofurane
derivative condensing this with 2-methyl-4-
amino-5-(thioformamido-ethyl) -pyrimidine.

REZSÖ KÖNIG.
ÁRPÁD GERECs.
ZOLTÁN FÖLDI.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF ALIPHATIC DICARBOXYLIC ACIDS

Walter Speer, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 1, 1941

The present invention relates to the production of aliphatic dicarboxylic acids, more particularly it relates to an improved process of preparing adipic acid and its higher homologues by the catalytic oxidation of cyclohexanone and its homologues.

In the preparation of dicarboxylic acids by oxidizing alicyclic ketones in the liquid phase by means of gaseous oxygen in the presence of oxidation catalysts, it has been found suitable to carry out the oxidation in the presence of a substantial amount of acetic acid which acts as a solvent. By this method of carrying out the preparation of adipic acids, which expression includes adipic acid itself and its higher homologues, generally part of the cyclohexanone which expression includes cyclohexanone and its homologues is decomposed to lower homologues of adipic acid, in particular to glutaric and succinic acid.

I have now found that the formation of lower homologues of adipic acid may be suppressed to a considerable extent, thereby increasing the yield of adipic acids, by carrying out the oxidation in a liquid containing from about 10 to about 40 per cent, preferably about 25 per cent of acetic acid. It is understood that the acetic acid content of the reaction mixture should not exceed 40 per cent and should not be below 10 per cent at any stage of the oxidation, i. e. at any stage of the process during which gaseous oxygen is allowed to pass through the reaction liquid.

The oxidation is carried out under conditions usually employed in the catalytic oxidation of ketones to carboxylic acids. Generally speaking, the temperature is kept within the range from about 40 to about 120° C. As catalysts there may be used, for example, copper, manganese, cobalt or vanadium and their salts, e. g. the acetates or nitrates. As oxidizing gases there may be used oxygen alone or air or oxygen in admixture with other inert gases different from nitrogen.

The oxidation may be carried out continuously, for example, by charging a tower with a mixture of acetic acid and cyclohexanone in the ratio 25 to 75 containing 0.1 per cent of a catalyst, e. g. manganese acetate, and passing a current of oxygen or air at 80° C through a porous filter plate at the bottom of the tower. Depending on the rate of the conversion of cyclohexanone into adipic acid, cyclohexanone is added, preferably through the oxygen- or air-inlet, thus avoiding that adipic acid is deposited on the filter plate. In order to separate adipic acid formed from the

reaction mixture, part thereof is withdrawn from the reaction vessel continuously or from time to time. The adipic acid crystallized out by allowing the solution to cool is filtered off or centrifuged, the cold mother-liquor being returned into the reaction vessel.

The crude adipic acid contains a small amount of acetic acid and of cyclohexanone. It may suitably be worked up in the following manner: The crude adipic acid is washed with part of the cyclohexanone which is to be introduced into the reaction vessel. Thus, the acetic acid contained in the crude adipic acid is removed and rendered useful in the oxidation thereby avoiding substantial losses thereof. The adipic acid now contains but a small amount of cyclohexanone which may be recovered by heating the adipic acid below its melting point and condensing the vapors emerging therefrom.

The adipic acid containing cyclohexanone may also be introduced slowly into nitric acid of sufficient strength to effect oxidation of cyclohexanone, e. g. 50 to 60 per cent nitric acid, heated to 60-70° C. The adipic acid is dissolved and the cyclohexanone oxidized forming adipic acid also dissolving in the nitric acid. By cooling the nitric acid, the adipic acid is obtained in the form of crystals. After washing with water, it is so pure that it may be employed directly for many technical purposes, e. g. for the preparation of hexamethylene diamine.

As already mentioned, the cyclohexanone admixed with the crude adipic acid may also be recovered wholly or partly by distillation. The adipic acid thus obtained may be recrystallized from water or nitric acid. On the other hand, the crude adipic acid freed from acetic acid but still containing cyclohexanone may be at once recrystallized from water, the cyclohexanone being separated from the aqueous solution and being returned into the reaction vessel.

It will be understood that the above given explanation of the reaction temperature, the catalysts and the method of carrying out the oxidation and the purification of the adipic acids is merely given for purpose of illustration and that the specific methods described are not an essential part of my invention but that numerous modifications of these methods may be made without departure from the spirit of my invention.

The invention will be described in greater detail in the following example which illustrates a typical embodiment of my invention. The in-

vention, however, is not restricted to this example.

Example

30 liters of oxygen per hour are introduced at 80° C into a mixture consisting of 100 grams of acetic acid, 300 grams of cyclohexanone, 0.3 gram of manganese acetate and 0.15 gram of barium acetate. Under these conditions, about 50 grams of cyclohexanone are oxidized per hour. This amount is continuously supplied by adding 50 grams of fresh cyclohexanone per hour. From time to time part of the reaction mixture is removed and allowed to cool. The adipic acid which deposits in the form of crystals is filtered off by suction and washed with cyclohexanone. The mother liquor and the cyclohexanone used for washing the adipic acid are returned into the reaction vessel.

The adipic acid is slowly introduced into twice its amount of 50 per cent nitric acid at 60° C, while cooling. The solution obtained is kept at 60° C for further 30 minutes and then allowed to cool. The adipic acid crystallized out is filtered off by suction and washed with 30 per cent of its amount of water. For 100 grams of cyclohexanone there are thus obtained 137 grams of adipic acid.

If carrying out the oxidation under otherwise identical conditions while starting from a mixture consisting of 70 per cent of acetic acid and 30 per cent of cyclohexanone, only 101 grams of

adipic acid are obtained for 100 grams of cyclohexanone.

The reaction may also be carried out with air as the oxidizing agent. In order to avoid losses of acetic acid, the spent gas should then be cooled vigorously or even washed with cyclohexanone. For example, the spent gases may be led through a tower through which cyclohexanone of low temperature is allowed to trickle.

The following table also shows the advantages residing in the use of a reaction mixture containing less than 40 per cent and more than 10 per cent of acetic acid. The amount of carbon dioxide formed corresponds to the rate at which adipic acid is converted into its lower homologues:

Composition of the reaction mixture		Percentage of CO ₂ in the total increase of weight of the reaction mixture
		Percent
300 grams of acetic acid	}	10
100 grams of cyclohexanone		
200 grams of acetic acid	}	6
200 grams of cyclohexanone		
100 grams of acetic acid	}	2.2
300 grams of cyclohexanone		
40 grams of acetic acid	}	6.5
360 grams of cyclohexanone		

WALTER SPEER.

ALIEN PROPERTY CUSTODIAN

HEAT-STABILIZED HIGH-POLYMER HALOGEN-CONTAINING PRODUCTS

Hans Fikentscher, Ludwigshafen-on-Rhine, and
Richard Roehm, Troisdorf-Oberlar, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 2, 1941

The present invention relates to high-polymer halogen-containing substances of improved heat-stability.

High-polymer substances containing halogen have a marked tendency to split off hydrogen halide on heating. The hydrogen halide so liberated not only causes discoloration of the substances but also attacks the metallic parts of the equipments in which the substances are worked, for example rollers or molds, and also metallic parts embedded in the finished molded articles made from the high-polymer substances.

It has been proposed to employ lead compounds as heat stabilizing agents. The poisonous effect of the lead compounds and their tendency to undergo discoloration in the presence of even slight quantities of hydrogen sulphide, however, prejudices their use in practice.

It is also well known to add basic substances, as for example alkali metal salts of weak organic acids, carbonates or hydroxides of the alkali or alkaline earth metals or organic nitrogenous compounds having a weak basic action, as stabilizing agents. These substances, indeed, absorb and neutralize the hydrogen halide split off in the heat, but, on the other hand, on account of their alkaline reaction, accelerate the splitting off of hydrogen halide in the heat from many high-polymer substances containing halogen so that in these cases completely colorless molded articles cannot be obtained. Ureas and thio-ureas too, which have been proposed as stabilizing agents, when added alone, do not prevent the high-polymer halogen-containing substances from becoming brown in the heat.

We have now found that the heat-resistance of high-polymer halogen-containing substances can be markedly improved by adding small amounts of alkaline substances and, in addition thereto, alcohols as stabilizing agents. As alkaline substances there may be mentioned the alkali metal and alkaline earth metal hydroxides and carbonates and salts of weak acids, especially of organic acids or of basic acid, furthermore basic phosphates.

Suitable alcohols are preferably the higher boiling alcohols, as for example dodecyl alcohol, octadecyl alcohol, phenylethyl alcohol, hydroxyethyl cresol and hydroxyethyl naphthol, dekahydronaphthol and hydroxydodekahydrodiphenyl, but low boiling alcohols may also be used.

Among high-polymer halogen-containing substances which can be stabilized according to our present invention may be mentioned, for example, chlororubber, polyvinyl chloride, chlorinated

polyvinyl chloride, polymeric as-dichlorethylene, polymeric chloracrylic compounds and inter-polymerization products of the monomeric compounds forming the basis of the above polymerization products, either among each other or with other polymerizable substances. The highly polymerized substances containing halogen may also contain softeners.

The stabilized high-polymer halogen-containing substances according to the present invention, are well resistant even when heated for a long time, having far less a tendency towards discoloration than when stabilized with the stabilizing agents hitherto proposed. While alkaline substances would also absorb and neutralize the hydrogen halide set free in the heat, their undesirable alkaline action is apparently lessened by the addition of an alcohol, so that they no longer tend to favor the splitting off of hydrogen halide.

The quantities of the alkaline substances and alcohols may vary within rather wide limits. Generally speaking, additions of from 0.1 to 1 per cent of the alkaline substance and of from 0.5 to 4 per cent of an alcohol are most suitable. There exists a definite rate of the stabilizing agents for each of the high-polymer halogen-containing substances exerting the best stabilizing effect, which rate may easily be ascertained by experiments.

The stabilizing agents may be added in a dissolved or suspended state or as a powder to the high-polymer halogen-containing substances, which may also be present in a dissolved, dispersed or solid state. In practice the stabilizing agents are most advantageously incorporated in the high-polymer halogen-containing substances as uniformly distributed as possible already before the substances are worked up in the heat, but the stabilizing agents may also be added while the substances are being worked in the heat, for example rolled or molded. In some cases the stabilizers may already be added to the high-polymer halogen-containing substances in the stage of their preparation, for example during their polymerization.

The present invention allows of heat molding high-polymer halogen-containing substances into completely colorless articles whereas the same articles hitherto obtained were more or less discolored.

The following example will further illustrate how the present invention may be carried out in practice, but the invention is not restricted to this example. The parts are by weight.

Example

100 parts of an interpolymerization product obtained by emulsion-polymerization of 95 parts of vinyl chloride and 5 parts of butyl acrylate which had been washed with sodium carbonate solution after precipitation and after drying still contained 0.3 per cent of sodium carbonate, are admixed with 3 parts of octodecyl alcohol in a ball mill. The polymerization product is then rolled on a hot roller at 165° C for 15 minutes and drawn off as a sheet having 0.1 millimeter

in thickness. The sheet is completely colorless and becomes slightly brown only after a two hours' storage at 155° C, whereas sheets made in the same manner but without the addition of octodecyl alcohol become brown already during the rolling.

The other alcohols enumerated above have the same effect.

HANS FIKENTSCHER.
RICHARD ROEHM.

ALIEN PROPERTY CUSTODIAN

METHOD OF STABILIZING ACTIVE
SUBSTANCES OF PLANTS

Alfred Kuhn, Dresden-Radebeul, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 8, 1941

The present invention relates to a method of stabilizing active substances, for instance volatile oils, alkaloids, hormones or vitamins existing in plants. The invention consists in this, that plants containing active substances are triturated with polysaccharides in a medium the acidity of which is controlled either by the presence of substances having an alkaline reaction, as sodium dicarbonate, mixtures of alkali phosphates or the like, or by substances having an acid reaction, as correspondingly determined electrolyte-buffer-mixtures or other acids or salts having an acid reaction or salt mixtures respectively, whereupon following the trituration drying is effected preferably at temperatures, which are not much higher than that of room temperature and under conditions at which the percentage of moisture of the drying air decreases with progressive temperature.

Under the term "polysaccharides" not only the pure chemical substances, as for instance starch, but also naturally existing mixtures, for instance potato flour, are to be understood. So, for instance, particularly the flour of bulbs of the *heleanthus tuberosus* has proved in practice to be an excellent agent for stabilizing volatile oils.

The preparation of triturations by the aid of trituration agents is well known. So for instance the U. S. Patent 2,128,616 discloses the preparation of triturations by the use of sugars as trituration agent, whereby also polysaccharides may be present. The quantity of these additions, however, is small with regard to the amounts of sugar serving as trituration agent, whereas according to the invention the trituration is carried out in such a manner that the polysaccharides as such must be considered to be the trituration agent. Whereas the known small additions of polysaccharides during the

production of sugar containing triturations act as accelerators of the drying process they have the capacity of fixing volatile active substances if they are present in preponderant quantities.

For this mode of operation it is essential, that the disintegration of the plant is effected together with the polysaccharides so that a polysaccharide aggregate is at once presented to each fracture surface of the plant and the volatile oil may be fixed by the polysaccharide.

One example of the method according to the invention is as follows:

From fresh branches of *juniperus sabina* 20% triturations with polysaccharides are carried out. As soon as the desired degree of fineness is reached, the trituration is dried in a current of air. In the example chosen, the water content of the fresh plant amounted to 50,6%, the oil content to 1,40%. If the relative oil content of the fresh plant is designated with 100 then it is proved that in the 20% trituration with *helianthus-tub-flour* 90,5% of the volatile oil are still found, a content which increases to 98,2% if the trituration is carried out in the presence of 2% of sodium carbonate. In the non-disintegrated plant the amount of volatile oil obtained is not as high as in the presence of the polysaccharides, because complete plants dried under the same external conditions resulted in obtaining 76,3% of the volatile oil only as is known also from the production of drugs.

The products obtained may be used for the most different purposes. The volatile oils may easily be obtained in pure state, as the volatile oil is present in enriched condition. They may, however, also be directly employed for curative purposes or other economical uses.

ALFRED KUHN.

ALIEN PROPERTY CUSTODIAN

METHOD FOR PRODUCING ANTIRACHITICALLY ACTIVE PREPARATION AND RESULTING PRODUCTS

Rezső Weisz, Budapest, Hungary; vested in the
Alien Property Custodian

No Drawing. Application filed May 9, 1941

This invention relates to a method for producing esters of antirachitic Vitamin. A. Windaus and O. Rygh (Nachr. v. d. ges. der Wissenschaften zu Göttingen, 1928, page 202) have examined the physiological activity of irradiation products of different ergosterol derivatives and have stated, as an unexpected result, that irradiated esters of ergosterol show only a weak, or no physiological activity, but these active irradiation products furnish, after saponification, products of high antirachitic activity. They have concluded therefrom that the presence of the unchanged hydroxyl group is necessary for the physiological activity, although they admit that some of the irradiated ergosterol esters, in the first place the irradiated ergosteryl-acetate, show a certain physiological activity.

I have proved that valuable preparations of antirachitic activity can be obtained by acetylating or esterifying of crystallized antirachitic Vitamin, e.g. Vitamin D₂ or Vitamin D₃ with other fatty acids.

The present invention consists in the preparation of antirachitically active products by esterifying crystalline antirachitic Vitamin with aliphatic carbonic acids preferably with fatty acids containing 14-18 carbon atoms. These ester preparations are characterized by their protracted activity. If the esterification of the crystalline Vitamin is carried out with fatty acids containing a high number of carbon atoms (14-18), e.g. with palmitic acid or stearic acid, products particularly distinguished by their physiological properties are obtained. These products injected

in oily solution or in suspensions show a slow and gradual resorption. The resorption which takes a long time and occurs step by step gives the possibility to supply the organism for months with the necessary quantity of antirachitic Vitamin; thus, these preparations are adapted not only for the curing but also for the prophylaxis of rachitis.

The following examples show how the process is to be carried out:

(1.) 2.9 g of crystalline Vitamin D₂ are dissolved in 5 ccs of pyridine and 5 ccs of acetic anhydride are added. After standing for 24 hours the reaction mixture is mixed with water and extracted with benzene. The benzene solution is then washed out with diluted acetic acid and afterwards with water. By evaporating the benzene one obtains 3.25 g Vitamin-D₂-acetate. The product is easily soluble in organic solvents.

(2.) 2.9 g of crystalline Vitamin D₂ are dissolved in 10 ccs of pyridine and 3 ccs of stearyl chloride are added. After standing for 2 days the reaction mixture is poured into water and extracted with ethyl acetate. The ethyl acetate solution is washed out with sodium carbonate solution of 1% and afterwards with water. By evaporating the solution 4.7 g of Vitamin-D₂-stearat are obtained. The product forms an oil and is easily soluble in organic solvents.

One proceeds similarly by starting from Vitamin D₁ or Vitamin D₃, or by starting from crystallized mixtures of different antirachitic vitamins.

REZSŐ WEISZ.

ALIEN PROPERTY CUSTODIAN

SUPERPOLYAMIDES AND PROCESS OF PRODUCING SAME

Hugo Kroeper, Heidelberg, Fritz Kohler, Mannheim, and Karl Wolf, Heidelberg, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 9, 1941

The present invention relates to superpolyamides and a process of producing same.

Superpolyamides, as is known for example from British Patent Specification No. 461,237, can be prepared by condensing certain diamines and dicarboxylic acids or derivatives or salts thereof or mixtures of these materials. The properties of the superpolyamides are dependant, in particular, on the degree of condensation and on the chemical nature of the diamines and dicarboxylic acids employed. The desired degree of condensation can be secured by employing definite temperatures and pressures during the condensation or by adding slight proportions of compounds capable of checking the growth of the chain of molecules in the condensation products, as for example primary amines, ammonia or organic monocarboxylic acids. Superpolyamides prepared in the presence of such additions do not undergo a further condensation upon heating as would be the case with superpolyamides prepared in the absence of such additions, which superpolyamides get tougher and tougher and contain an increasing amount of vapor bubbles when melted for a prolonged time and can therefore in certain cases be worked, for example spun, only with difficulty.

We have now found that superpolyamides which are heat-resistant, i. e. are no longer subject to further condensation and can therefore be well worked, in particular well spun in the molten state, are obtained by condensing about molecular proportions of superpolyamide-forming dicarboxylic acids and diamines in the presence of up to 20 per cent by weight (calculated with regard to the final superpolyamide) of a glutaric acid diamine salt. The superpolyamides thus obtained also possess a high gloss which is often desirable for films and threads. An addition of 10 per cent. of glutaric hexamethylenediamine

salt to adipic acid hexamethylenediamine salt, for example yields a superpolyamide which melts only about 30° C below the superpolyamide from adipic acid hexamethylenediamine salt alone, and can be kept in the molten state for a long time without its viscosity becoming higher and bubbles being developed, i. e. without undergoing further condensation. Though glutaric acid diamine salts, when condensed alone, only yield brittle products giving but fragile threads when spun, the loss of mechanical strength is surprisingly small with additions up to 20 per cent according to our invention and especially at 10 per cent and below (calculated with reference to the final superpolyamide) and the practical use of the superpolyamides is not interfered with thereby.

The following Example serves to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said Example. The parts are by weight.

Example

100 parts of glutaric acid hexamethylenediamine salt and 900 parts of adipic acid hexamethylenediamine salt are heated to 280° C in a pressure-tight vessel of chromium-nickel steel, after the air having been eliminated by means of free nitrogen. The pressure produced by the water formed in the condensation is released after at least one hour's heating, whereupon heating is continued at from 280° to 285° C for 4 hours. The melt of superpolyamide formed is then forced through a nozzle into water. The superpolyamide obtained is well fusible and can be easily spun from the melt without leaving any residue.

HUGO KROEPER,
FRITZ KOHLER.
KARL WOLF.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF OXALKYLATION PRODUCTS

Heinrich Hopff, Wilhelm Muenster, and Josef
Stadler, Ludwigshafen-on-Rhine, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 13, 1941

The present invention relates to a process for the production of oxalkylation products.

We have found that valuable oxalkylation products are obtained by causing polyamides or superpolyamides (under which term we comprise polycondensation products of compounds capable of yielding acid amides) to react with alkylene oxides.

As polyamides and superpolyamides suitable for the purposes of the present invention we mention those which are obtainable from ω,ω' -diamines and dicarboxylic acids or from aminocarboxylic acids. For example the polyamides or superpolyamides from tetramethylenediamine, pentamethylenediamine, hexamethylenediamine or aliphatic diamines of a still higher molecular weight, or mixtures of these diamines and succinic acid, glutaric acid, adipic acid, pimelic acid or dicarboxylic acids of a still higher molecular weight or mixtures of such dicarboxylic acids are suitable. Polyamides and superpolyamides obtainable by the polycondensation of glycol and higher aminocarboxylic acids, such as aminocaproic acid, or their lactams, or mixed condensation products are also well adapted for being reacted with alkylene oxides.

The reaction can be practiced by heating the polyamides or superpolyamides together with one or several alkylene oxides, for example with ethylene oxide or propylene oxide, preferably while using the alkylene oxides in an excess quantity, in a closed vessel, or by introducing the alkylene oxides into the molten polyamides or superpolyamides or their solutions in organic solvents. The reaction generally takes place already at comparatively low temperatures, for example at between 80 and 150°C. In the case of melts higher temperatures must be used, depending on the melting point of the initial materials.

By the treatment with alkylene oxides polyalkylene-glykol radicles are introduced into the polyamide or superpolyamide molecules. Depending on the quantity and the type of the alkylene oxide and on the nature of the initial material used products of varying properties are obtained. Generally speaking, the oxalkylation will lower the melting point and increase the solubility in water.

The products obtained by the oxalkylation of polyamides and superpolyamides are adapted for quite a variety of applications, for example as softeners for plastics, especially those obtained from polyamides and superpolyamides. With great success they may be used as softeners for films or film-like structures of water sensitive

cellulosic materials such as regenerated cellulose. They can also be used for the improvement of textiles, paper, leather and other fibrous materials, especially artificial fibres; for these latter purposes oxalkylation products from polyamides or superpolyamides which are soluble or readily dispersible in water are especially suitable. They are, for instance, useful as finishing, sizing, equalizing, softening, dispersing or impregnating agents. They may be employed by the manner commonly known in using other textile assistants for similar purposes.

The following examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to these examples. The parts are by weight.

Example 1

10 parts of a polyamide obtained by heating an 80 per cent aqueous solution of 1 mol of ϵ -aminocaprolactam for 5 hours in the presence of $\frac{1}{50}$ mol of acetic acid is heated, after removing the water by distillation, with 50 parts of ethylene oxide at from 100 to 120°C for 12 hours. After distilling off the excess ethylene oxide a swollen gelatinous mass is left behind, the chief part of which dissolves in water and which is suitable for use as an adhesive or softener for plastics and as a thickening agent for printing pastes.

Example 2

10 parts of a mixed polyamide obtained by the mixed condensation of 50 parts of hexamethylenediammonium adipate with 50 parts of ϵ -aminocaprolactam are heated with 100 parts of ethylene oxide at from 120 to 150°C for 15 hours. After removing the excess ethylene oxide a faintly yellowish jelly remains which dissolves in water forming a clear solution. When replacing the ethylene oxide by an equivalent amount of propylene oxide, products showing similar properties are obtained.

Example 3

100 parts of the high-molecular pulverulent product obtainable by heating 1 mol of hexamethylene diisocyanate with 1 mol of 1,4-butylene glycol in the presence of orthodichlorobenzene are heated together with 500 parts of ethylene oxide to 150° C for 10 hours. A yellow viscous oil is obtained which dissolves in alcohols forming clear solutions.

Example 4

Untreated skeins of viscose artificial silk are treated in a bath (at a ratio of 1:20) containing

1 gram of the product according to Example 2 to each liter, at room temperature, whereupon the material is centrifuged and dried. By this treatment the artificial silk is imparted a full and soft touch, otherwise obtainable only with products prepared on a fatty acid basis.

Example 5

Skeins of viscose artificial silk are treated in a bath containing per liter 75 grams of the oxalkylation product employed in Example 4, at room temperature, centrifuged and dried, whereby an excellent sizing effect is obtained. Each thread of the so treated artificial silk is perfectly closed, elastic and resistant to mechanical treatment so that it is very well adapted for weaving. The size can easily be removed by means of warm water. The sizing effect is equal to one obtained with a size from linseed oil from benzine solution, but the size obtained according to this invention stands storage and does not resinify.

Example 6

Cotton is dyed with 0.5 per cent of Indanthrene Brilliant Green 5G (cf. G. Schulz, Farbstofftabellen 1931, Nr.1269) as usual in a bath which contains 0.25 gram of the oxalkylation product employed in Example 4 per each liter of bath. A very uniform dyeing is thus obtained.

Example 7

Woollen cloth is dyed with 3 per cent of a com-

plex chromium compound of an acid dyestuff and from 5 to 10 per cent of sulphuric acid in a bath (ratio 1:50) which contains per each liter 1 gram of the oxalkylation product according to Example 2, at boiling temperature for 1 hour. A well developed, very uniform dyeing is obtained which is perfectly fast to rubbing.

Example 8

The oxalkylation product according to Example 2 is dissolved in water of 40 degrees hardness (German scale) at the rate of 0.5 gram to each liter, whereupon soap is added to the solution at the rate of 2 grams to each liter. While the solution shows slight turbidity, there is no precipitation of lime soap.

Similarly may soap solutions be rinsed out of textile materials by admixing each liter of the hard water with which rinsing is done with 0.5 gram of the product according to Example 2. Lime soap which has already precipitated can also be redissolved by the addition of the said product.

Similar results are obtained by using another oxalkylation product of a polyamide or superpolyamide, for example an equal amount of the oxethylation product of the polyamide or superpolyamide from ϵ -aminocaprolactam or from adipic acid and ω,ω' -diaminooctane.

HEINRICH HOPFF.
WILHELM MUENSTER.
JOSEF STADLER.

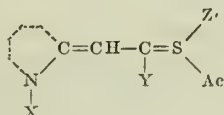
ALIEN PROPERTY CUSTODIAN

INTERMEDIATES FOR DYESTUFFS

Willem Mees, Mortsel, near Antwerp, Belgium;
vested in the Alien Property Custodian

No Drawing. Application filed May 20, 1941

This invention relates to the preparation of intermediates for dyestuffs, constituted most probably according to the following formula:

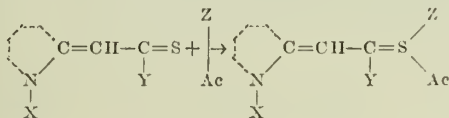


is some nitrogen containing ring nucleus, such as for instance thiazole, selenazole, or the like, which may be further substituted by alkyl, phenyl or phenylene or other polynuclear rings, while Z and X represent alkyl or a substituted alkyl such as for instance aralkyl, Y represents alkyl, a substituted alkyl such as for instance an aralkyl or phenyl, and Ac represents any acid radical, such as for instance halogen, alkyl sulphate, toluene-sulphonate or the like.

According to the invention, now these compounds can easily be prepared by reacting the thioketones (described in an application filed of even date herewith by Polydoor de Smet and myself, as joint inventors), under the influence of heat, with an ester of the general structure Z-Ac, wherein Z and Ac have the meaning given above. In this reaction the ester is simply fixed to the thioketone.

The condensation can also be carried out in the presence of a solvent for the thioketone such as for instance toluene or benzene, and is preferably effected by heating the components under a reflux condenser.

The reaction is believed to take place according to the following equation:



wherein the symbols used have the meaning given above.

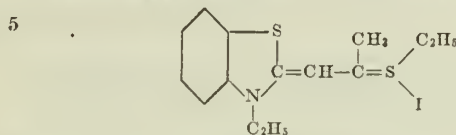
My invention is however not defined by this equation, nor limited by it; it is essentially characterised by the new method of preparation and by the specific compounds obtainable thereby.

These intermediates are fit for use in the preparation of symmetrical and asymmetrical carbocyanines, which are substituted at the central carbon atom of the methine chain.

To this end, the new compounds are heated in the presence of an acid binding agent with 2-alkyl substituted quaternary salts. The dyestuff condensation proceeds under the formation of a mercaptan of the general formula HS-Z and an acid of the formula HAC.

Example I

In the preparation of the intermediate product characterised by the following probable formula:

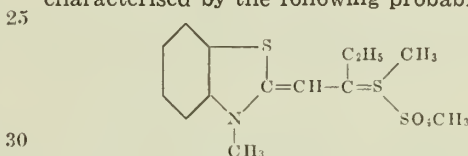


23 gr. N-ethyl-benzthiazolidene-methyl-methylthioketone and 18 gr. ethyliodide are heated 1 hour under the reflux condenser in a boiling water bath. The mixture is shaken repeatedly whereupon it solidifies. After cooling it is washed with dry ether. The yield is 29 gr. (73% of the calculated amount). After recrystallization from ethylalcohol small grey-brown needles are obtained, which melt at 228° to 230° C under decomposition.

Determination of S: 16.04% (calculated 16.36%).

Example 2

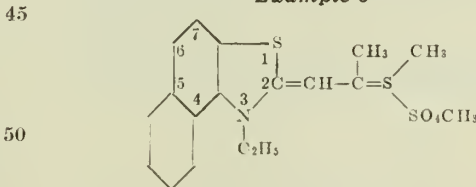
The preparation of the intermediate product characterised by the following probable formula:



To 23 gr. N-methylbenzthiazolidene-methyl-ethylthioketone suspended in 100 cc. dry benzene are added 14 gr. dimethylsulphate and the mixture is shaken several times and heated 1 hour under the reflux condenser in a boiling water bath. After cooling, the mass is filtered by suction, washed with acetone and dried. The yield is 33 gr. (93% of the theoretical). After recrystallization from a mixture of alcohol and acetone small brown-yellow needles are obtained which melt at 190° C.

Determination of S: 26.66% (calculated 26.59%).

Example 3

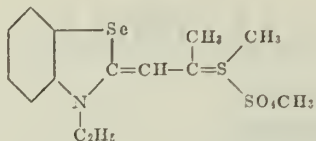


To 23 gr. N-ethyl-4-5-benzo-benzthiazolidene-methyl-methylthioketone suspended in 150 cc. dry benzene are added 14 gr. dimethylsulphate and the mixture is heated under repeated shaking 1 hour under the reflux condenser in a boiling water bath. After cooling, the mass is filtered by suction and washed with a little acetone. The yield is 23 gr. (66% of the calculated amount).

After recrystallization from alcohol small, light yellow, silky needles are obtained, which melt at 213-214° C.

Determination of S: 23.35% (calculated 23.3%)

Example 4

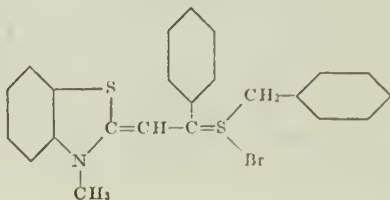


To 28 gr. N-ethyl-benzselenazolidene-methyl-methylthioacetone dissolved in 100 cm. benzene are added 14 gr. dimethylsulphate and the mixture is heated under repeated shaking 1 hour under the reflux condenser in a boiling water bath. After cooling the precipitate is filtered by suction and washed with a little acetone.

The yield is 31 gr. (77% of the calculated amount).

After recrystallization from alcohol small, light yellow needles are obtained. Melting point at 174°.

Example 5

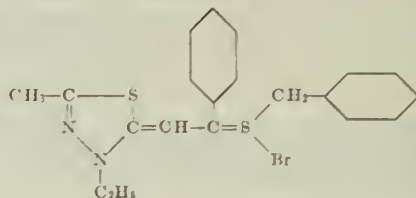


56 gr. finely divided (N-methyl-benzthiazolidene-

methyl) phenylthioacetone and 35 gr. benzylbromide are thoroughly mixed and heated during one hour at 110° C. The solid mass is purified by washing with acetone. Recrystallization from a mixture of acetone and methylalcohol gives yellow crystals, melting by decomposition from 155° to 176° C.

Determination of S: 14.35% (calculated amount: 14.1%).

Example 6



52 gr. finely divided (N-ethyl-5-methyl-thiodiazolidene-methyl)-phenylthioacetone and 35 gr. benzylbromide are strongly mixed and heated for one hour at 110° C. The crude product is washed with acetone, and after recrystallization from a mixture of acetone and methylalcohol are formed yellowish crystals, melting by decomposition from 135° to 155° C.

Determination of S: 14.80% (calculated amount: 14.75%).

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

WILLEM MEES.

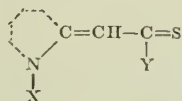
ALIEN PROPERTY CUSTODIAN

INTERMEDIATES FOR DYESTUFFS

Polydoor De Smet and Willem Mees, Mortsel, near Antwerp, Belgium; vested in the Alien Property Custodian

No Drawing. Application filed May 20, 1941

This invention relates to the manufacture of intermediates for dyestuffs of the general formula:



wherein X is an alkyl or a substituted alkyl, such as for instance aralkyl, Y is an alkyl or a substituted alkyl, such as for instance aralkyl or phenyl or other aryl while the group



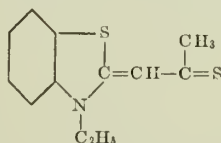
represents any nitrogen containing nucleus such as for instance thiazole, selenazole or the like which may be substituted by alkyl, phenyl, phenylene or any polynuclear ring.

These new substances, which may be considered as being thioketone derivatives of heterocyclic compounds, readily react with reactive alkyl- or methylene groups under formation of hydrogen sulphide, so that they are useful intermediates in the preparation of dyestuffs, such as symmetrical and asymmetrical carbocyanines or merocyanines.

These thioketones can also be used in the preparation of other intermediates for dyestuffs.

According to the invention these new compounds are prepared by reacting acid halides with 2-alkyl derivatives of quaternary cyclammonium salts in the presence of sulphur-splitting compounds such as phosphorus pentasulphide, preferably in an acid-binding solvent such as for instance pyridine.

Example 1.—Preparation of (N-ethyl-benzthiazolidene-methyl)-methylthioketone:



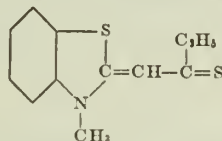
350 g 2-methyl-benzthiazol-ethyl-toluenesulphonate and 150 g phosphorus pentasulphide are thoroughly mixed. To this mixture are added 1300 ccm dry pyridine, which previously have been cooled to below 5° C. After recooling under 5°, 100 g acetylchloride are slowly added, the temperature being kept below 5°. After ¼ hour the temperature is allowed to rise to room temperature under repeated shaking and the whole is finally heated ½ hour in a boiling water bath.

The pyridine is evaporated in vacuo and the dark-brown colored residue washed with water; during the washing the product solidifies. After thorough drying in a vacuum-dessicator it is recrystallized from benzine (boiling point 120/140° C). The yield is 48.5 g (20%).

After recrystallization from ethyl alcohol, yellow brown needles are obtained which melt at 146° C.

Determination of S: 26, 73%. Calculated amount: 27, 2%.

Example 2.—Preparation of (N-methyl-benzthiazolidene-methyl)-ethylthioketone.



275 g 2-methyl-benzthiazol-dimethylsulphate and 150 g phosphorus pentasulphide are thoroughly mixed. To this mixture are added 1300 ccm cold, dry pyridine.

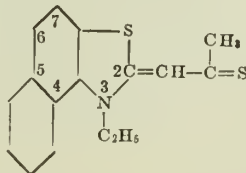
After cooling to below 5° C, 120 g propionylchloride are slowly added, the temperature being kept below 5° C. After ¼ hour the temperature is allowed to rise to room temperature under repeated shaking and the reaction mixture is finally heated ½ hour in a boiling water-bath.

The pyridine is evaporated under reduced pressure and the dark-brown colored residue washed with water; during washing the product solidifies. After thorough drying in a vacuum-dessicator, the crude product is recrystallized from benzine (boiling point 120°/140° C). The yield is 95 g (40%).

After recrystallisation from ethyl alcohol, yellow needles, melting at 155°–156°, are obtained.

Determination of S: 27.7%. Calculated amount: 27.23%.

Example 3.—Preparation of (N-ethyl-4-5-benzo-benzthiazolidene-methyl)-Methylthioketone:



400 g 2-methyl-4-5-benzo-benzthiazol-ethyltoluene-sulphonate and 150 g phosphorus pentasulphide are thoroughly mixed. To this mixture are added 1500 ccm dry pyridine, which were cooled to below 5° C. After recooling below 5° C, 100

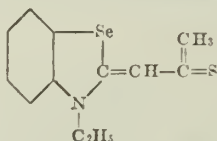
g acetylchloride are added gradually, the temperature being always held below 5° C. After ¼ hour the temperature is allowed to rise to room temperature and finally the mixture is heated ½ hour in a boiling water-bath.

The pyridine is evaporated in vacuo and the dark-brown residue washed with water. The solidified product is dried in a vacuum-dessicator and recrystallized from benzine (boiling point: 120°/140°).

Recrystallization from ethyl alcohol gave yellow brown needles, melting at 194° C.

Determination of S: 22.8%. Calculated amount: 22.5%.

Example 4.—Preparation of (N-ethyl-benzselenazolidene-methyl)—methyl thioketone:



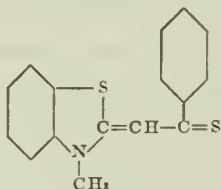
To a mixture of 350 g 2-methyl-benzselenazolidene-ethyl iodide and 150 g phosphorus pentasulphide are added 2000 ccm cold, dry pyridine. After re-cooling below 5° C, 100 g acetylchloride are slowly added, the temperature being held below 5° C. After ¼ hour the temperature is allowed to rise to room temperature under repeated shaking and the reaction mixture is finally heated ½ hour in a boiling water-bath.

The pyridine is distilled off in vacuo and the dark-brown colored residue washed with water; during washing the crude product solidifies. After thorough drying it is recrystallised from benzine (boiling point 120°/140°). The yield is 90 g (32%).

After recrystallising it from ethyl alcohol, brown-red needles, melting at 136°–138°, are obtained.

Example 5

Preparation of (N-methyl-benzthiazolidene-methyl)-phenyl-thioketone



275 grams finely divided 2-methyl-benzthiazolidene-dimethyl-sulfate and 150 grams phosphorus pentasulphide are mixed with 1000 ccm cold, dry

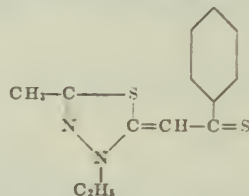
pyridine. The mixture is chilled below 5° C and 175 g benzoylchloride are slowly added under good stirring and cooling. After ¼ hour the temperature is allowed to rise to room temperature and under repeated shaking the mixture is finally heated half an hour in a boiling water bath under the reflux condensor. After evaporation of the pyridine in vacuo, the dark colored residue is treated with cold water until it becomes a solid mass. After thorough washing and drying in a dessicator it is recrystallized from benzine (boiling point 120°/140°). The yield is 168 g (59%).

Recrystallization from ethylalcohol yielded yellow needles, melting at 176° C.

Determination of S: 21.19% (calculated amount: 22.61%).

Example 6

Preparation of (N-ethyl-5-methylthiodiazolidene-methyl)-phenyl-thioketone



To a finely divided mixture of 270 g 2-5-dimethyl-thiodiazolidene-ethyl iodide and 150 g phosphorus pentasulphide are added 1000 ccm cold, dry pyridine. Under good stirring and cooling, to keep the temperature of the reaction mass below 5° C, 175 g benzoylchloride are gradually added. After about 15 minutes the temperature is allowed to rise to room temperature and the whole is then heated ½ hour in a boiling water bath under a reflux-condenser.

The pyridine is removed by evaporation under reduced pressure and the red-colored residue is washed with water. It is filtered by suction and dried at low temperature. On recrystallizing the crude product from ethylalcohol, the yield is 165 grams (63%).

Further recrystallization from alcohol gives light-red colored crystals, melting at 165° C.

Determination of S: 24.45% (calculated amount: 24.42%).

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

POLYDOOR DE SMET.
WILLEM MEES.

ALIEN PROPERTY CUSTODIAN

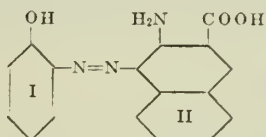
COMPLEX CHROMIUM COMPOUNDS OF AZO DYE STUFFS

Karl Mueller, Ludwigshafen-on-Rhine, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 23, 1941

The present invention relates to complex chromium compounds of azo dyestuffs.

I have found that valuable complex chromium compounds of azo dyestuffs are obtained by treating in substance azo dyestuffs of the formula



wherein the nuclei marked I and II may contain further substituents, with agents capable of yielding chromium.

The starting materials are obtainable by diazotizing an ortho-aminophenol which preferably contains at least one additional substituent, such as halogen or a nitro, alkyl, alkoxy or sulfonic acid group, and combining the diazo compound with 2-aminonaphthalene-3-carboxylic acid or a substitution product thereof being free in the 1-position. Suitable coupling components are for example 2-aminonaphthalene-3-carboxylic acid-5- or 6-sulfonic acid.

The complex chromium compounds may be prepared by heating the metal-free dyestuff with a chromium compound, e. g. chromic formate or chromic chloride, in aqueous or organic solution or suspension, if desired under superatmospheric pressure. The chromium may also be introduced into the azo dyestuffs by heating them in a melt prepared from a carboxylic acid amide or the ammonium salt of a carboxylic acid and containing a compound of trivalent chromium.

The complex chromium compounds thus obtained by chromination in substance, i. e. in the absence of fibres, are characterized in that they contain one atom of chromium for each molecule of the dyestuff. Chromination on the fibre, however, leads to the formation of chromium compounds containing two atoms of chromium for three molecules of the dyestuff.

The new complex chromium compounds, prepared in substance, are capable of dyeing animal fibres, e. g. wool or silk, or synthetic fibres having the properties of animal fibres, clear green shades. The dyeings are very level and excellently fast to light, water, perspiration, steam and hot-ironing. Chrome-tanned leather is dyed deep green shades which are very fast to washing and water. The complex chromium compounds derived from dyestuffs free from sulfonic acid groups or the salts prepared from chromium compounds of dyestuffs containing sulfonic acid groups and organic bases may be used for dyeing cellulose ester

lacquers, plastic compositions or acetate artificial silk spinning solutions.

The following examples will further illustrate how my invention may be carried out in practice.

5 The invention, however, is not restricted to these examples. The parts are by weight.

Example 1

23.4 parts of 1-amino-2-hydroxy-3-nitrobenzene-5-sulfonic acid are diazotized in the usual manner at 15° C. The diazo solution is then rendered acid to litmus by adding thereto 15 parts of sodium acetate. A weakly alkaline solution of 20.5 parts of 2-aminonaphthalene-3-carboxylic acid, heated to 75° C, is allowed to flow into the diazo solution, the whole being kept at 50° C until coupling is completed. The azo dyestuff formed is salted out, filtered off and washed. The dyestuff is admixed with water to form a paste, the latter being heated with a chromium formate solution, containing 20 parts of chromic oxide and 20 parts of formic acid, for 4 hours to 130° C under superatmospheric pressure. The complex chromium compound deposits in the form of a dark powder when allowing the reaction mixture to cool. It dyes wool and silk clear green shades of good fastness.

A similar dyestuff yielding somewhat bluer shades may be prepared in the same manner from the azo dyestuff derived from diazotized 1-amino-2-hydroxy-5-nitrobenzene-3-sulfonic acid and the same coupling component.

Example 2

35 The diazo solution obtained from 15.4 parts of 1-amino-2-hydroxy-4-nitrobenzene is added in acetic acid solution at 50° C to a solution of 30 parts of 2-aminonaphthalene-3-carboxylic acid-6-sulfonic acid. The azo dyestuff formed is salted out, filtered off by suction and dried. It is dissolved in 250 parts of formamide at 110° C. 27 parts of chromic chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) are added, and the melt is heated to 120° C for 2 hours and to 130° C for one further hour. The whole is then poured into water whereby the chromium containing dyestuff is precipitated out. It dyes chrome-tanned leather clear green shades of good fastness to washing and water. Wool and silk are dyed vivid green shades.

50 Similar dyestuffs are obtained when employing 1-amino-2-hydroxy-4-nitro-5-chlorobenzene or 1-amino-2-hydroxy-3-nitrobenzene-5-sulfonic acid as diazo components.

KARL MUELLER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF β,β' -
DICYANO DIETHYL ETHER

Heinrich Hopff and Wilhelm Rapp, Ludwigs-
hafen-on-Rhine, Germany; vested in the Alien
Property Custodian

No Drawing. Application filed May 23, 1941

The present invention relates to a process for the production of β,β' -dicyano-diethyl ether. It has already been described that by adding aromatic and aliphatic compounds which contain hydroxyl groups on to α,β -unsaturated nitriles, β -cyano-alkyl ethers are obtained as the addition products.

We have now found that by reacting acrylic nitrile with water β,β' -dicyano-diethyl ether is obtained in a very good yield; i. e. by the addition of 2 mols of the acrylic nitrile on to 1 mol of water a dinitrile comprising an oxygen bridge in the carbon chain is formed according to the following equation:

$$2\text{CH}_2=\text{CH}-\text{CN}+\text{H}_2\text{O}\rightarrow$$
$$\text{NC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CN}$$

The reaction takes place at a comparatively low temperature, preferably at about 20° to about 80° C in the presence of small amounts of an alkaline catalyst, such as the alkali metal and alkaline-earth metal hydroxides and the alkali metal and alkaline-earth metal salts of weak acids. It is preferable to add to the reaction mix-

ture a small quantity of a stabilizer inhibiting the polymerization of the unsaturated nitrile, as for example hydroquinone.

The following example serves to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said example. The parts are by weight.

Example

A mixture of 106 parts of acrylic nitrile, 18 parts of water, 0.05 part of hydroquinone and 0.3 part of pulverised sodium hydroxide is stirred at between 55° and 60° C for about 2 hours. The reaction mixture is then neutralized with dilute sulphuric acid, whereupon the aqueous layer is separated and the oily reaction product is distilled. After a first runnings of a slight amount of unconverted acrylic nitrile, 22 parts of β,β' -dicyano-diethyl ether pass over at from 150° to 155° C. under a pressure of 1.5 millimeters (mercury gauge).

HEINRICH HOPFF.
WILHELM RAPP.

ALIEN PROPERTY CUSTODIAN

PROCESS OF PREPARING MONOCHLORO-MONOBROMOMETHANE

Otto Scherer and Franz Dostal, Frankfurt am Main, and Karl Dachlauer, Hofheim am Taunus, Germany; vested in the Alien Property Custodian

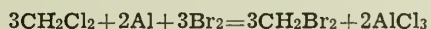
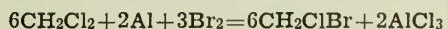
No Drawing. Application filed May 23, 1941

The present invention relates to a process of preparing monochloromonobromomethane and dibromomethane.

It is known that by reaction of aliphatic chlorinated hydrocarbons with aluminium bromide 5 chlorine may be exchanged for bromine and aliphatic brominated hydrocarbons may be obtained. Since the preparation of aluminium bromide is, however, rather complicated and its handling is not agreeable, it would be of considerable advantage for the industrial preparation of brominated hydrocarbons if instead of $AlBr_3$ elementary 10 bromine and aluminium could be used. The pertaining art discloses only poor and contradictory statements about the results of this method of working. It is stated that besides worthless resinous products brominated hydrocarbons are mainly obtained which do not correspond with the chlorinated hydrocarbons used as parent materials.

Indeed, experiments with numerous aliphatic chlorinated hydrocarbons, also with those still containing hydrogen in the molecule, have shown that the exchange of chlorine for bromine by using bromine and aluminium instead of aluminium bromide encounters great difficulties. 25 Considerable quantities of resinous by-products or reaction products of high molecular weight are formed which render the process unsuitable.

Now, we have found as a surprising fact that 30 the exchange of chlorine for bromine in halogen-methane compounds still containing two hydrogen atoms, namely in the methylene chloride and the monochloromonobromomethane, takes a very smooth course when bromine and aluminium are used and that only an unimportant quantity of by-products is formed. The exchange takes place according to the following equations:



A smooth course of these reactions could not be expected all the less since, as it is known, methyl chloride reacts easily with aluminium with formation of organometallic compounds, choloform reacts with aluminium with formation of undefined resinous products and carbon tetrachloride reacts with aluminium with formation of hexachlorethane. Monochloromonobromomethane also reacts easily with aluminium with entire transformation into resinous products of high molecular weight.

For the reaction of the said halogenated hydrocarbons in which chlorine is to be exchanged for

bromine it is advantageous to use a sufficient excess of the halogenated hydrocarbon so that the reaction liquid remains well stirrable with the sludgy aluminium chloride obtained. It has, furthermore, proved to be advantageous to add somewhat larger quantities of aluminium than those calculated stoichiometrically in order to attain that the reaction liquid contains no longer free bromine when the reaction is finished.

In the preparation of monochloromonobromomethane from methylene chloride by simultaneous action of bromine and aluminium on methylene chloride, the formation of dibromomethane may be the more repressed; the larger the excess of the methylene chloride used is in proportion to the aluminium and bromine, respectively. 15

The following examples serve to illustrate the invention but they are not intended to limit it thereto:

(1) Preparation of monochloromonobromomethane from methylenechloride. 20

500 grams of methylenechloride and 60 grams of aluminium in the form of shavings or waste of sheets are placed into a vessel provided with a reflux apparatus, a feeding device for bromine, a thermometer and a stirrer and, without stirring, 25 grams of bromine are caused to run in so that the bromine forms a bottom layer. After a few minutes, reaction sets in which becomes more and more vivid and which becomes apparent by the fact that boiling begins and the temperature rises quickly. When the temperature in the reaction liquid attains about $35^\circ C$, further 1000 grams of methylene chloride are caused to run in so quickly that the temperature does not fall too much. By adding, while stirring, further 455 grams of bromine in such a degree that the reaction mixture is kept gently boiling, the reaction is kept alive. When all the bromine has been introduced, the reaction mixture has a boiling point of about $47^\circ C$. Stirring is continued for a short time, advantageously while slightly heating. The reaction liquid no longer contains free bromine and the aluminium used, with the exception of a few grams, is transformed into a fine sludge of aluminium chloride. 45

The whole batch is cast on ice and the mixture of halogenated hydrocarbons is driven off by means of steam. The mixture of halogenated hydrocarbons which has been separated from the water and dried is worked up by fractional distillation. There are obtained:

	Grams
Recovered methylene chloride-----	970
Monochloromonobromomethane-----	590
Dibromomethane-----	75
Distillation residue-----	15

(2) By working up in a corresponding manner a batch prepared by means of, all in all,

there are obtained besides unchanged monochloromonobromomethane 520 grams of dibromomethane.

	Grams
Monochloromonobromomethane-----	1164
Aluminium-----	33
Bromine-----	240

OTTO SCHERER.
FRANZ DOSTAL.
KARL DACHLAUER.

ALIEN PROPERTY CUSTODIAN

COMPOSITIONS OF MATTER

Arthur Voss, deceased, late of Frankfurt am Main, by Hedwig Voss, administratrix, Frankfurt am Main, Germany, and Karl Dietz, Kronberg im Taunus, and Heinz Thomas, Hofheim am Taunus, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 23, 1941

The present invention relates to compositions of matter.

It is known that, owing to their mechanical strength and chemical resistance, the so-called phenol resins, i. e. condensates from phenols and formaldehyde, are dominating among the plastics known in the art though they belong to one of the oldest classes of plastics and though they lack one important property, namely the elasticity characteristic of a series of new plastics, for instance, polymerization products.

Whereas the polymeric plastics possess an elasticity very similar to that owned by their natural prototypes, the cellulose and the caoutchouc, the plastics from phenol and formaldehyde show in their final state, i. e. in the case of hardenable resins in the state of resites, a comparatively small elasticity. Therefore, wherever this property is required in the industry said plastics can hardly be applied with success. In this domain, therefore, the phenol resins had to give way to the highly elastic plastics obtained by polymerization.

Since, however, the polymers do not live up to certain other properties of the phenol resins, the problem of preparing elastic phenol resins became more and more urgent; yet all attempts to arrive at a really satisfactory solution were without success. One of these attempts, repeated in vain, was the combination of phenol resins with softeners. Most of the softeners, however, had an insufficient compatibility with phenol resins and those which were sufficiently compatible and gave rise to an improved elasticity were also not suitable since the improvement attained was again lost when the phenol resin was converted into its final state, i. e. the resite. The ingredients of the mixture demixed and the masses lost their uniformity and, consequently, their elastic properties.

Now, we have found that elasticity may be imparted to phenol resins by mixing them, if condensed not further than to the resol state and if being capable of hardening when heated or when mixed with known hardening agents, with long-chained aliphatic organic compounds containing at least 12 carbon atoms and having in their molecule both an exchangeable, that is to say a reactive, halogen and a hydrophilic group. Substances of this kind may belong to various classes of compounds; there are suitable, for instance, halogenhydrins, that is to say long-chained aliphatic compounds containing in their molecule bound to adjacent carbon atoms, on the one hand, an OH-group and, on the other hand, a

halogen atom. Furthermore, there are very suitable halogen containing polymerizates containing in the molecule besides the halogen atom a carboxylic acid group, the latter being present either as such or in the form of its anhydride. Such polymeres are, for instance, interpolymers from vinylchloride and maleic anhydride, from vinylchloride and acrylic acid and from vinylchloride and methacrylic acid. Instead of vinylchloride, vinylchloracetate may be interpolymerized with the said monomeric acids. There may, furthermore, be used interpolymerizates from chloromaleic anhydride and vinyl compounds such as styrene, vinylacetate. In all these polymeres the halogen is very reactive. Such interpolymerizates are, for instance, described in Patent Specification No. 2,047,398.

The above mentioned substances which are all long-chained organic compounds and possess besides a very reactive halogen atom a hydrophilic group may be incorporated with the phenolaldehyde resins in various ways. It is possible to add the additional substances already during the manufacture of the phenolaldehyde resins or to admix them to the primarily formed liquid precondensates from phenol and aldehyde which are obtained in the usual manner by means of alkaline condensing agents and which still are in the resol state. It is also possible to use the said substances as additions to pulverulent masses from which moulded articles are to be prepared. Furthermore, the said substances may be added to known mixtures of phenol and aldehyde which harden in the cold or to liquid pre-condensated from phenol and aldehydes with simultaneous addition of the usual catalysts of hardening action, especially those of acid reaction, and/or adjuvants improving the chemical resistance. Catalysts of hardening action are described in U. S. Patent No. 2,034,802; for this purpose aromatic sulfochlorides are particularly useful. Adjuvants improving the chemical resistance of the said compositions of matter after hardening are, for instance, aliphatic esters of inorganic acids, as described in patent application Serial No. 241,016 filed November 17, 1938, in the name of Karl Dietz, Heinrich Greune and Franz Privinsky for "Masses capable of hardening rapidly in the cold and process of preparing them".

The above mentioned additional substances are distinguished from all hitherto known agents used for hardening in the cold or for improving the elasticity by the fact that they impart to the products considerably better elastic properties. These final products may be obtained in

various forms, as masses for preparing shaped or moulded articles or, if desired with filling agents, as cement or mortar masses or as lacquers or the like.

The following examples serve to illustrate the invention but they are not intended to limit it thereto, the parts being by weight:

(1) 80 parts of a normal pulverulent phenol-formaldehyde-resin mass are mixed with 20 parts of an interpolymersate from vinylchloride and maleic anhydride. This mixture may be used without any further treatment for the preparation of moulded articles of all kinds especially by way of hot-pressing. The elastic properties are essentially better than those of the articles obtained from normal phenol-resin masses, without the other known valuable properties of the phenoplasts being reduced.

(2) 90 parts of a liquid artificial resin obtained by condensation of phenol and formaldehyde are mixed with 10 parts of a chlorhydrin obtained from epichlorhydrin and dodecyl alcohol. The mixture may be hardened either by heat or by addition of a substance having a hardening action in the cold, for instance, an aromatic sulfochloride. An addition of softeners, for instance, benzyl alcohol, is also possible. These mixtures may be used either for lacquer-like paints or for impregnating building material

and wood; furthermore, in admixture with filling agents, as mortar for building masonry, for pointing and plastering or for preparing coatings, adhesives and filling-in masses.

Instead of the above mentioned chlorhydrin there may also be used the chlorhydrin obtained from epichlorhydrin and lauryl alcohol.

(3) 50 parts of a liquid condensation resin obtained from phenol and formaldehyde are mixed with 20 parts of an interpolymersate from vinylchloride and maleic anhydride or of an interpolymersate from chloromaleic anhydride and vinyl acetate as well as with 20 parts of 1,3-dichloropropanol and 10 parts of benzyl alcohol. 40 parts of this mixture are mixed with 10 parts of benzene sulfochloride whereupon the whole mass hardens by itself in the cold. Instead of benzene sulfochloride there may also be used paratoluene sulfochloride.

The mixtures thus obtained which harden in the cold may be used, with filling agents, for the preparation of mortars, cements and filling-in masses or, without filling agents, diluted with solvents for lacquers and impregnations.

HEDWIG VOSS,
As Administratrix of Arthur Voss, Deceased.
KARL DIETZ.
HEINZ THOMAS.

ALIEN PROPERTY CUSTODIAN

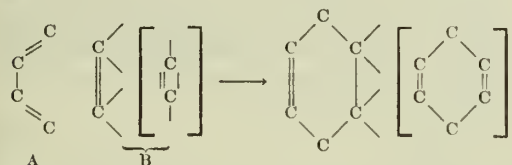
CONDENSATION PRODUCTS

Kurt Alder and Hans-Ferdinand Rickert, Cologne, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 24, 1941

The present invention relates to new condensation products and to the process of preparing the same.

The so-called "diene-synthesis" resides in the addition of compounds containing two conjugated C=C double linkages with such compounds containing an ethylene or acetylene group wherein the said unsaturated linkage is likewise conjugated with another double bond. In general, the "diene-synthesis" proceeds in the following manner.



it being to be understood that in the reaction component designated by symbol B the unsaturated linkage is activated by another double bond as stated above. Examples for compounds of type B are 1,3-dienes, α,β -unsaturated aldehydes, ketones, carboxylic acids and carboxylic acid nitriles.

The present invention is based on the observation that the "diene-synthesis" is not restricted to the situations as defined above. We have found that certain unsaturated compounds containing a single C=C double linkage which is not activated by another unsaturated bond, are likewise capable of forming addition products of the character described, if reacted upon with compounds containing two conjugated C=C double linkages. Starting materials of the first type are vinyl esters of organic acids, vinyl halogenides, dihalogen and trihalogen ethylenes. Compounds of the latter type are those commonly employed in the diene-synthesis such as butadiene-1,3, isoprene, 2,3-dimethylbutadiene-1,3, cyclopentadiene, cyclohexadiene and anthracene.

The reaction is performed by simply heating the mixture of the starting materials, preferably in a closed vessel. As a matter of fact care must be taken that the reaction is performed under such conditions as to prevent any substantial polymerization. To this end, polymerization inhibitors such as hydroquinone, pyrogallol and the like may be added to the reaction mixture, particularly in case of working with butadiene-1,3, isoprene and 2,3-dimethylbutadiene. As stated above, the reaction is performed at an elevated temperature, it being impossible to give definite lower and upper limits, since the optimum reac-

tion conditions depend on the nature of the starting materials and on the tendency of the butadienes and the like to form dimeric products. In general, the dimerization process occurs more slowly than the addition of the 2 reaction components. On the other hand, some of the dimeric products may be split up into the monomeric products at a high temperature, whereas the addition products formed by the interaction of the 2 reaction components are stable at such temperatures. Thus, in case of cyclopentadiene the reaction is preferably performed at 180° C as at this temperature the dimerics are split up so that the addition process is nearly quantitative. Other dienes such as anthracene do not show any tendency to form dimerics at the usual reaction temperature.

This application is a divisional of our application Ser. No. 246,492, filed December 17, 1938.

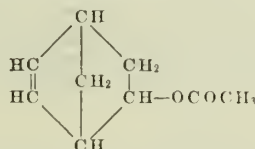
The following examples illustrate the present invention without, however, restricting it thereto, the parts being by weight unless otherwise stated:

Example 1

100 parts of freshly distilled monomeric cyclopentadiene and 150 parts of vinyl acetate are heated in an autoclave for 14 hours to 180-190°. After distilling off at normal pressure the excess vinyl acetate, the reaction mixture is subjected to distillation in vacuo. At 11 mm pressure the following three fractions are obtained:

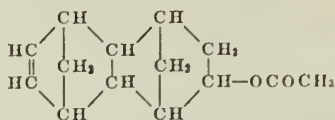
	Parts
I: 73-77°	100
II: 77-140°	10
III: 140-150°	48

Fraction I represents the addition product of the components in the proportion 1:1. It has an intensively ester-like smell and corresponds to the following constitution of a Δ^3 -norbornylene-ol-1-acetate:



By saponification there is obtained the hitherto unknown alcohol, viz. the Δ^3 -norbornylene-ol-1 of the melting point 108-109°. The hydrotriazole prepared therefrom by the addition of phenylazide has the melting point 147-148°. By hydrogenation of the alcohol in an acetic acid solution with platinum oxide the α -norborneol is obtained which is described in Annalen der Chemie, Vol.

512, 172 (1934). Fraction III represents the addition product of 2 mols of cyclopentadiene and 1 mol of vinyl acetate. The said compound corresponds to the following constitution:



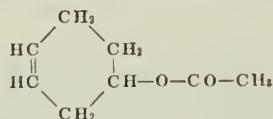
By saponification with methylalcoholic potassium hydroxide there is obtained therefrom the corresponding unsaturated alcohol of melting point 83°, which yields with phenylazide a hydrotriazole of melting point 194–195°.

Example 2

When replacing in the preceding example the 150 parts of vinyl acetate by 100 parts of vinyl formiate and working under the same conditions, the formiates of the two alcohols are obtained in form of colorless oils of boiling point 75–80° (at 20 mm pressure) or 140–143° (at 20 mm pressure) respectively.

Example 3

When heating equal parts by volume of butadiene-1,3 and vinyl acetate with the addition of polymerization inhibitors for 12 hours in an autoclave and distilling off the reaction mixture in vacuo, there is obtained besides some unchanged vinyl acetate and dimeric butadiene the addition product of the components, i. e. the Δ^3 -cyclohexane-ol-1-acetate in form of a colorless oil of boiling point 173–175° which corresponds to the following formula:



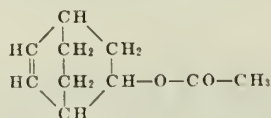
This compound, if subjected to catalytic hydrogenation takes up the amount of hydrogen corresponding to one double linkage, cyclohexanol acetate being formed thereby. By saponification with alcoholic potassium hydroxide the cyclohexanol of boiling point 155–156° is obtained therefrom, the phenyl urethane of this alcohol showing a melting point of 82°.

Example 4

When replacing in Example 3 the butadiene by 2,3-dimethyl butadiene and working up in the usual manner there is obtained the 3,4-dimethyl- Δ^3 -cyclohexene-ol-1-acetate in form of a colorless oil of an intensively ester-like smell which on saponification with methylalcoholic potassium hydroxide is converted into the corresponding alcohol (phenyl urethane of melting point 112° C).

Example 5

By the addition of $\Delta^{1,3}$ -cyclohexadiene and vinyl acetate there is obtained, when working according to the preceding examples, the bicyclic acetate of the following constitution:

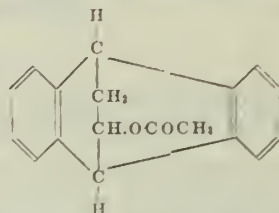


which is converted into the corresponding unsaturated alcohol (phenylurethane of melting point 125–126°) by saponification with methylalcoholic potassium hydroxide.

Example 6

10 parts of anthracene in 120 parts of xylene are heated in an autoclave for 18 hours to 220–230° with the addition of 20 parts of vinyl acetate. The reaction being complete, the solvent and the excess vinyl acetate are evaporated whereby the residue partly crystallizes; on sucking off and rinsing with methanol the precipitate proves to be identical with unchanged anthracene (1 part).

After a short time the methanol containing mother liquor forms a mass of crystals which represent the addition product of the components. On dissolving from alcohol colorless crystals of melting point 101° C are obtained which probably correspond to the following constitution:



On saponification the ester yields the corresponding alcohol of melting point 142°.

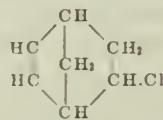
Example 7

80 parts of vinyl chloride and 80 parts of cyclopentadiene are heated in an autoclave for 15 hours to 170–180°. On distilling off the unchanged vinyl chloride the residue is fractionated in vacuo. At 11 mm pressure the following two fractions are obtained:

	Parts
I: 46–47°	73
II: 128–131°	28

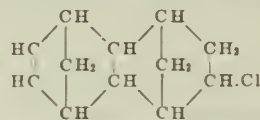
Fraction I represents the chloride of the following constitution:

The hydrotriazol which is obtained therefrom by



the addition of phenylazide melts at 115–116°.

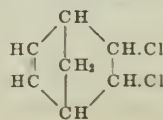
Fraction II represents the addition product of 2 mols cyclopentadiene and 1 mol of vinyl chloride of the following constitution:



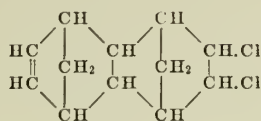
With phenylazide a hydrotriazol of melting point 195° is obtained.

Example 8

By a 15 hours' heating of 175 parts of 1,2-dichloroethylene with 125 parts of cyclopentadiene in an autoclave and after distilling off the reaction product in vacuo at 11 mm pressure as described in example 7, there are obtained the following two addition products of 1 or 2 mol of cyclopentadiene and 1,2-dichloroethylene:



of boiling point 74-76° at 11 mm pressure; the hydrotriazol shows the melting point 148°;
and

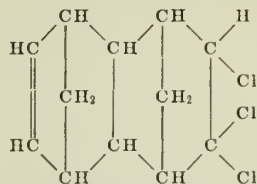


of boiling point 146–148° at 11 mm pressure; the hydrotriazol shows the melting point 210°.

Example 9

When adding trichloro-ethylene to cyclopentadiene while heating the components in an autoclave at 175–185° the addition product of 2 mols

of the latter and the trichloroethylene of the following constitution is obtained:



This compound represents a colorless oil which boils in vacuo at 11 mm pressure at 158–160°. With phenylazide it yields a hydrotriazole of melting point 225–226°.

KURT ALDER.

HANS-FERDINAND RICKERT.

ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCTS AND PROCESS OF PRODUCING SAME

Rudolf Kern, Ludwigshafen-on-Rhine, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed May 29, 1941

The present invention relates to new condensation products and a process of producing same.

I have found that new soluble nitrogenous condensation products can be obtained by treating, if desired in the presence of alcohols or phenols, with formaldehyde the products obtainable by condensing aliphatic amines containing two primary amino groups separated from each other by a chain of at least 5 carbon atoms which may be interrupted by hetero atoms, such as oxygen, and the nitrogen of imino groups, with carbonyl compounds, i. e. aldehydes and/or ketones, which condensation products are difficultly soluble in water and organic solvents. The conversion of the said difficultly soluble products (which expression—wherever used herein—includes insoluble products), especially those obtainable from the aliphatic diamines and formaldehyde, into soluble ones by the treatment with formaldehyde can be combined with their production into one operation. As initial materials there may be mentioned, for example, the completely or partly insoluble condensation products from penta-, hexa-, octo-, deka-, undeka- or dodeca-methylenediamine or mixtures of such diamines on the one hand and formaldehyde, crotonaldehyde, butyraldehyde, succinic dialdehyde, benzaldehyde, terephthalaldehyde, acetone, benzophenone or mixtures of such aldehydes and/or ketones on the other hand. For example, I may use the completely or partly insoluble products described in the copending U. S. application Ser. No. 338,374 filed on June 1, 1939, in the names of Heinrich Hopff, August Weickmann and Rudolf Kern. Condensation products prepared from the said components with the coemployment of urea, thiourea, dicyanodiamidine or melamine, can also be treated in the manner described.

For rendering soluble the insoluble condensation products it is preferable to employ from 1 to 5 mols of formaldehyde per each molecule of difficultly soluble initial material, but the invention is not restricted to working with such amounts. It is frequently of advantage to perform the treatment in the heat, but simple mixing with formaldehyde is sufficient in many cases, especially if the initial materials are freshly prepared. It is advantageous to effect mechanical agitation of the reaction mixture. The formaldehyde is preferably employed in the form of aqueous solutions of usual concentration, but other forms, for example, anhydrous trioxymethylene, may also be employed. The reaction may be carried out in the presence of alcohols, for example ethyl, propyl, butyl, benzyl alcohol, cyclohexanol

as well as of alcohol mixtures, for example mixtures of the said alcohols or of alcohol mixtures, such as are obtained in the reduction of low-molecular fatty acids from the paraffin wax oxidation, or in the catalytic hydrogenation of carbon monoxide under pressure. Phenols, too, may be present.

The new products which are soluble in water and/or organic solvents, as alcohols, esters, ketones and aromatic hydrocarbons, are not changed by further condensation during storage. In part they yield lacquer films which when hardened by means of acid hardeners and/or by heating possess great surface hardness, excellent elasticity, resistance to water and stability to solvents. The products can also be employed as binding agents in printing, coating or impregnating paper, textiles or metals, as adhesives, for example in the leather or wood industry, as thickening agents or binders for aqueous paints or finishes. The water-soluble products are also suitable for rendering textile materials crease-proof or animalizing them.

The following Examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said Examples. The parts are by weight.

Example 1

1400 parts of an aqueous 30 per cent solution of formaldehyde is run into a mixture of 812 parts of hexamethylene-diamine and 7300 parts of water at room temperature, while stirring. The white insoluble condensation product formed is filtered off by suction, washed with water, sharply squeezed off, dried at between 80° and 100° C in vacuo and ground. It is colorless, very voluminous and elastic and practically insoluble in any solvent. It is heated to boiling for from 4 to 6 hours with three times its amount (by weight) of a 30 per cent aqueous formaldehyde solution. The aqueous solution formed can be used with advantage for rendering cell-wool or artificial silk fabrics crease-proof. In the case of cell-wool it effects an improvement of the rubbing fastness both in the dry and wet state, which properties are retained also when the material is boiled with water.

Example 2

48 parts of the insoluble condensation product from hexamethylenediamine and formaldehyde referred to in Example 1 are dissolved in a mixture of 60 parts of an aqueous solution of formaldehyde of 30 per cent strength and 200

parts of butanol by heating for three hours at 90° C while stirring. From the solution obtained the water and the butanol are removed by evaporation in vacuo; a very pale resin is thus obtained which can be drawn into threads and when dissolved in butanol yields a high-quality lacquer of excellent elasticity, surface hardness and resistance to water, and which may be employed, for example, for coating metal surfaces. Advantageously this lacquer is baked at from 100° to 120° C. The reaction product can be freed from butanol also by evaporation in vacuo. It then furnishes similar effects on cell-wool materials as the product according to Example 1.

If 120 parts of formaldehyde solution are used instead of 60 parts, there is formed a bottom layer consisting of water and excessive formaldehyde, whereas the resin remains dissolved in butanol. After separating off the bottom layer, the top layer is worked up in the manner described above.

Example 3

1 mol of crotonaldehyde and 1.3 mols of formaldehyde are caused to react with 1 mol of hexamethylenediamine in an aqueous medium. The insoluble reaction product which is obtained in a highly swollen state is treated with four times its amount of a 30 per cent solution of formaldehyde and with butanol while stirring and heating. The solution thus obtained is suitable for lacquer purposes.

Example 4

To a suspension of 60 parts of urea in 300 parts of butanol there are added at ordinary temperature 200 parts of a 30 per cent. aqueous solution of formaldehyde. To the solution obtained a solution of 58 parts of hexamethylenediamine in 100 parts of butanol is added at a batch while vigorously stirring. After a short time the solution spontaneously warms to about 60°C with formation of a stiff jelly which is passed into solution by the addition of another 200 parts of 30 per cent formaldehyde while heating. The pale resin obtained by evaporating the solution is soluble in water, alcohol and butanol and useful for various technical purposes. Paints prepared therewith are rendered insoluble by baking. As hardeners substances having an acid reaction, such as hydrochloric acid, magnesium chloride or ammonium chloride, may be added.

A similar product is obtained by substituting thiourea for urea.

Example 5

100 parts of the still liquid product resulting from the condensation of equimolecular proportions of ω,ω' -diamino-di-n-propylether of butanediol-1.4 ($\text{H}_2\text{N} \cdot \text{C}_3\text{H}_6 \cdot \text{O} \cdot \text{C}_4\text{H}_8 \cdot \text{O} \cdot \text{C}_3\text{H}_6 \cdot \text{NH}_2$) and crotonaldehyde (which condensation goes on with the separation of water) are passed into solution by the addition of 250 parts of a 30 per cent aqueous solution of formaldehyde and 200 parts of butanol.

Example 6

116 parts of hexamethylenediamine and 384 parts of cyclohexanol are heated together at from 100 to 115°C while stirring, whereupon a mixture of 150 parts of aqueous formaldehyde of 30 per cent strength and 100 parts of cyclohexanol is added drop by drop. The water of the formaldehyde solution and the water formed in the reaction are continuously removed during the condensation by azeotropic distillation. After 12 hours' stirring at the said temperature, the reaction mixture is heated at from 140° to 150°C for about 30 minutes. The reaction product is a pale, completely clear, viscous solution yielding films which dry in the air and by baking may have their properties yet improved. They are remarkable for their resistance to water and elasticity. Instead of the formaldehyde solution there may be employed 50 parts of trioxymethylene.

When mixing the hexamethylenediamine with cyclohexanol at ordinary temperature, the addition of formaldehyde will yield an insoluble white condensation product which becomes soluble by further reaction with formaldehyde, for example while heating in the manner described above.

Example 7

232 parts of hexamethylenediamine and 200 parts of phenol are fused together. 300 parts of a 30 per cent aqueous solution of formaldehyde are run in at between 100 and 150°C with agitation and the water is removed by azeotropic distillation. The reaction mixture is then heated for 4 hours at from 150 to 170°C. The reaction product being soluble in ethanol, butanol, butylacetate and benzene is a tough resin suitable for lacquer purposes as well as for rendering textiles crease-proof.

RUDOLF KERN.

ALIEN PROPERTY CUSTODIAN

CAPILLARY ACTIVE AGENTS

Winfried Hentrich, Rodleben B. Dessau-Rosslau,
Heinz-Joachim Engelbrecht and Erik Schirm,
Dessau, Germany; vested in the Alien Property
Custodian

No Drawing. Application filed June 6, 1941

Capillary active agents

This invention relates to capillary active agents and process of making same.

It has been found that valuable capillary active agents can be produced by treating compounds having the general formula



with acylating or alkylating agents which comprise at least three carbon atoms in the molecule. In this general formula Ar denotes an aromatic hydrocarbon residue which may eventually also comprise core substituents such as for instance halogene-hydroxyl-, alkyl-, alkoxy-residues or the like or a second amino-residue; preferably Ar denotes an eventually substituted benzol-residue.

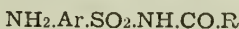
The residues X and Y denote either both the radical SO_2 or one of them the radical SO_2 and the other the radical CO.

R denotes an aliphatic or an aromatic hydrocarbon residue which may eventually be substituted.

For the production of the capillary active agents there are preferably used aminoaryl compounds following the general formulae



or

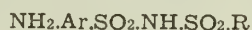


The following are examples of amino-aryl compounds of the general formula referred to: N-(3-amino-benzol-sulphonyl)-acetamide, N-(3-amino-4-chlor- or -4-alkoxy-benzol-sulphonyl)-acetamide, N-(3-amino-4-methyl-benzol-sulphonyl)-propionamide, N-(4-amino-benzol-sulphonyl)-butyryl-amide, N-(3-amino-benzol-sulphonyl)-lauramide, N-(3-amino-benzol-sulphonyl)-benzamide, N-(3- or -4-amino-benzoyl) methane-sulphamide, N-(3-amino-4-methyl-benzoyl)-benzol-sulphamide, N-(3'-amino-benzoyl)-3-amino-benzol-sulphamide, N-3'-amino-4-methoxy-benzoyl)-4-amino-benzol-sulphamide, and the like.

The amino compounds mentioned are produced in the familiar way, for example by acting with aryl-sulphonamides, or salts thereof, the aryl residue of which contains a group capable of conversion into an amino group, on aliphatic or aromatic carbonic acid chlorides. Upon completion of the reaction, the amino groups are formed from the groups that permit of conversion into an amino group, for which latter the acylamino groups and nitro groups chiefly come into consideration. The aromatic amino compounds

mentioned can further be produced by the action of aromatic carbonic acid chlorides, the aromatic residue of which contains groups capable of conversion into amino groups, on aliphatic or aromatic sulphonic acid amides, whereby the amino groups are thereafter similarly formed in the condensation product.

For the production of the capillary active agents there may further be used aromatic amino compounds following the general formulae



and



Such aromatic amino compounds are for instance 3-amino-benzol-benzol sulphimide, 3-amino-benzol-4'-methyl-benzol-sulphimide, 3-amino-benzol-methane-sulphimide or another 3-amino-benzol-alkan-sulphimide, 3-amino-benzol-benzol-sulphimide-3'-carbonic acid, 3,3'-diamino-dibenzol-sulphimide or its core substitution products, such as for instance halogen-, hydroxyl-, methyl-, ethyl-, methoxy-, ethoxy-, phenoxy-, amino-substituted products and the like. These amino-diaryl-sulphimides, for instance, can be obtained by the conversion of aryl-sulphochlorides, which contain in the aryl residue a group which is convertible into an amino group, with alkyl- or aryl-sulphamides, and by subsequent conversion of the group which is convertible into an amino group, that is, for instance, of a nitro- or acyl-amino group into the amino group. Also the opposite way may be followed by converting aryl-sulphamides which comprise in the aryl residue a group convertible into an amino group with alkyl- or aryl-sulphochlorides and by subsequently forming the amino group. In either case known processes are used.

According to this invention these aromatic amino compounds are acted upon by acylating or alkylating agents which comprise at least 3 C-atoms and about up to 18 C-atoms in the molecule. The action of the acylating or alkylating agents on the aromatic amino compounds takes place according to methods which as such are known.

The acylating agents that chiefly come into consideration are the fatty acids and their functional derivatives, such as for example, fatty acid anhydrides, fatty acid esters, fatty acid halogenides, and the like, and further organic sulphonic acid halogenides. Esters of chlorated carbonic acid, isocyanates, isothiocyanates, and chlorides of urea further come into consideration. The following alkylating agents may be mentioned:—

halogen alkyls, halogen alkylating products of alcohols, carbonic acid and sulphonic acid amides, sulphuric acid or aryl-sulphonic acid esters of compounds with aliphatically combined hydroxyl groups, and the like. The foregoing alkylating and acylating agents may also contain lipophile residues of higher molecular weight, i. e., aliphatic hydrocarbon residues with at least six carbon atoms, or cyclo-aliphatic or aromatic hydrocarbon residues which possess a side chain of at least three hydrocarbon atoms.

As examples of these acylating and alkylating agents we mention the following: propionic acid, butyric acid, capric acid, a mixture of coconut oil fatty acids, oleic acid, palmitic acid, mixtures of any fatty acids, naphthenic acid, resin acids, acetyl chloride, acetic acid anhydride, stearic acid chloride, montanic acid chloride, cetyl-sulphonic acid chloride, stearyl-sulphonic acid chloride, chlorated carbonic acid dodecyl ester, chlorated carbonic acid hexadecyl ester, octylisocyanate, dodecyl-isothiocyanate, N-carbonyl-palmitic acid amide, N-carbonylstearic acid-amide, N-carbonyl-cetyl-sulphonic acid amide, N-carbonyl-stearyl-sulphonic acid amide, dodecyl-urea chloride, and the like. The following may be mentioned as examples of alkylating agents: propyl chloride, octylchloride, dodecyl chloride, octylchloride dodecyl chloride, dodecyl-chloromethyl-ether, hexadecyl - chlor - methyl-ether, and the like. The hydrocarbon residues of these agents belonging to the aliphatic or cyclo-aliphatic series or mixtures of these two series, or to the fatty aromatic series, may also contain familiar hetero-atoms or heteroatomic groups, or substitutes thereof, such, for example, as halogen, hydroxyl groups, and so on, as is the case, for example, with octyl-hydroxy-acetyl chloride, or iso-octyl-phenoxy-acetyl chloride.

The agents referred to may act on the aromatic amino compounds according to familiar methods in an aqueous medium or in the presence of organic solvents, according to the initial products used. If necessary, an elevated temperature may be applied for the reaction, and further, as far as necessary, agents that bind water or acid. For example, acylation by means of carbonic acids may also be carried out in toluol solution in the presence of phosphorus trichloride or thionyl chloride. In order to facilitate the reaction, these amino group may previously be converted into an isocyanate group upon which these fatty acids are allowed to act, whereby reaction takes place while carbonic acid is split off.

For the production of the capillary active agents from aromatic amino compounds of the general formula $\text{NH}_2\text{.Ar.SO}_2\text{.NH.SO}_2\text{.R}$ mainly acylating agents come into question, which may also contain higher molecular lipophile residues, that is aliphatic or cyclo-aliphatic hydrocarbon residues of at least six hydrocarbon atoms in the molecule or aromatic hydrocarbon residues having side chains of at least three carbon atoms.

The compounds obtained by the process forming part of the present invention are of the general formula R'.NH.Ar.X.NH.Y.R . In this formula Ar, X, Y, R denote the above mentioned substances. Accordingly, R is an aliphatic or an aromatic residue. In the latter case the residue may also comprise an amino substitute which has been alkylated or acylated. R' denotes an alkyl residue or an acyl residue.

By acyl residue there is understood the residue R.CO as well as the residue R.O.CO (from

chlor carbonic acid esters) and R.NH.CO (from chlorides of urea or isocyanates).

Thus, the capillary active agents produced according to this invention may have the general formulae $\text{R'.NH.Ar.CO.NH.SO}_2\text{.R}$ or



Such compounds are, for instance, N-(3-lauroyl-amino-benzol-sulphonyl)-benzamide, N-(3-palmitoyl-amino-benzoyl)-methane-sulphamide, N-(3'-capronoyl-amino-benzoyl)-3-capronoyl-amino-benzol-sulphamide, N-(3-propionyl-amino-benzol-sulphonyl)-benzamide, N-(3-butyryl-amino-benzol-sulphonyl)-benzamide, N-(3'-capronoyl-amino-benzol-sulphonyl)-benzamide, N-(3-capryloyl-amino-benzol-sulphonyl)-propane-sulphamide, N-(3-caprinoyl-amino-benzol-sulphonyl)-octane-sulphamide, N-(3'-capryloyl-amino-benzoyl)-3-capryloyl-amino-benzol-sulphamide, N-(3'-caprinoyl-amino-benzoyl)-3-caprinoyl-amino-benzol-sulphamide, N-(3-capronoyl-amino-benzol-sulphonyl)-benzamide, N-(3-caprylyl-amino-benzol-sulphonyl)-propane-sulphamide, and N-(3-caprinyl-amino-benzol-sulphonyl)-octane-sulphamide.

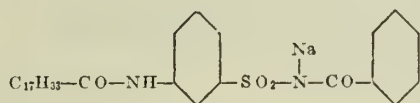
Furthermore, the capillary active substances produced according to this invention may be of the general formula $\text{R'.NH.Ar.SO}_2\text{.NH.SO}_2\text{.Ar.NH.R'}$. Such compounds are for instance 3-lauroyl-amino-benzol-benzol-sulphimide, 3-lauroyl-amino-benzol-methane-sulphimide, 3,3'-dicapryloyl-amino-dibenzol-sulphimide, 3-capronoyl-amino-benzol-methane-sulphimide, 3-capryloyl-amino-benzol-methane-sulphimide, 3-caprinoyl-amino-benzol-methane-sulphimide, 3-palmitoyl-amino-benzol-methane-sulphimide, 3,3'-dicapronoyl-amino-dibenzol-sulphimide, 3,3'-dicaprinoyl-amino-dibenzol-sulphimide.

The compounds obtained by the process forming part of this invention are amorphous bodies and are possessed of surface-active properties. They also are possessed of a considerable detergent and frothing property, even if the residues that have been introduced by acylation or alkylation are of a relatively low molecular character. The optimum of detergent property is present in such compounds in which the hydrocarbon residue R' comprises about from 6 to 10 carbon atoms. The compounds, therefore, may advantageously be employed in connection with washing, cleaning, wetting, dispersing and emulsifying processes, such as are customary in the textile and laundry-industry, fur-industry, leather-industry and other industries. The products may be used as such or also in combination with known washing and cleaning agents or as an addition to such agents.

Example 1

276 parts by weight of N-(3-amino-benzol-sulphonyl)-benzamide are dissolved in 1500 parts by weight of water with the addition of 40 parts by weight of sodium hydroxide. After adding 200 parts by weight of crystallized sodium acetate, the solution is cooled to 2 degr. C and a mixture of 300 parts by weight of oleic acid chloride and 300 parts by volume of acetone are stirred in at a temperature of 2 to 5 degr. C. Stirring is kept up for half an hour at 2 degr. C, 500 parts by weight of water are added, and the whole is treated with 20 percent soda solution until litmus paper shows a neutral reaction. Condensation is completed by heating the reaction mixture for one hour at 50 degr. C. The clear, thickish so-

lution is then diluted with 3000 parts of water and 1250 parts by weight of common salt are added; as soon as the salt has dissolved, the mixture is cooled to about 5 degr. C. The precipitate is removed by pressure or centrifuging and dried at 100 degr. C. It represents an amorphous mass that dissolves in water, producing a heavy froth. The yield of the condensation product is between 85 and 90 percent of the theoretical. Its formula is

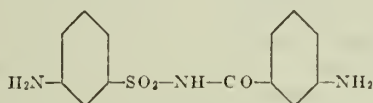


Example 2

276 parts by weight of N-(3'-amino-benzoyl)-benzol-sulphamide are dissolved in 1500 parts by weight of pyridine and the solution is cooled to 2 degr. C. Then 240 parts by weight of lauric acid chloride diluted with an equal volume of acetone are stirred in at 2 to 5 degr. C; stirring is kept up for one hour at ordinary temperature, which is then raised to 50 degr. C and 10 percent soda solution is cautiously added until litmus paper shows a permanently alkaline reaction. The reaction mixture is then distilled under considerably reduced pressure, the dry residue is dissolved in the requisite quantity of hot water, and the condensation product is isolated by salting out, filtering when cold, and drying. The mass can be pulverized and dissolves in water giving rise to froth. The yield is similar to that of Example 1.

Example 3

An aqueous solution of the sodium salt of 291 parts by weight of N-(3'-amino-benzoyl)-3-amino-benzene-sulphamide of the formula



is prepared as described in Example 1. After having added 300 parts by weight of crystalline sodium acetate, 350 parts by weight of caprylic acid chloride are gradually added at 0 to 5 degr. C. After neutralization with soda, the reaction is completed by heating to 50 degr. C, as described in the foregoing Example 1, and the condensation product is recovered in excellent yield, as there described, by salting out, filtering, and drying. In spite of the fact that the alkyl residues are of comparatively low molecular weight, the product possesses remarkably good detergent properties.

Example 4

236 parts by weight of the sodium salt of N-(3-amino-benzene-sulphonyl)-acetamide, 250

parts by weight of n-dodecyl bromide, 30 parts by weight of magnesium oxide, 1200 parts by weight of alcohol, and 1200 parts by weight of water are heated for six hours at 150 degr. C in an autoclave fitted with a stirrer. The reaction liquid is filtered, while still hot, to the filtrate is added hydrochloric acid, and the bright amorphous precipitate after cooling is removed by suction, filtered and dried. The product is of a waxy nature and dissolves easily in hot dilute soda solution while frothing.

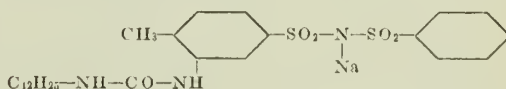
Example 5

155 parts by weight of thionyl chloride are caused to trickle under stirring at a temperature of about 30° C into a mixture consisting of 164 parts by weight of 3,3' diamino-dibenzol-sulphimide, 150 parts by weight of caprylic acid and 900 parts by weight of toluol; the mixture is thereupon heated for some hours at the reflux cooler to boiling condition. On ceasing development of gas the non-dissolved reaction product is separated by suction and washed with toluol. The residue is dissolved in soda solution, precipitated by means of diluted hydrochloric acid and recrystallized from alcohol (melting point at 173° C). By treatment with soda lye the formed 3,3'-dicapryloyl-amino - dibenzol - sulphimide is converted into the sodium salt which is soluble in water yielding vigorously frothing solutions.

By replacing the caprylic acid by a mixture of fatty acids (C₇—C₉) having an acid number 390, which mixture is obtained by oxidation of the paraffine, there will result a product having similar properties.

Example 6

215 parts by weight of dodecyl-isocyanate are caused to trickle well cooling into a solution consisting of 326 parts by weight of 4-methyl-3-amino-benzol-benzol-sulphimide and 900 parts by weight of pyridine; the mass is subsequently stirred for some time at 50° C. On removing the pyridine by distillation the residue is worked in the manner stated in Example 1 and converted into the corresponding sodium salt. There will be obtained a good yield of a condensation product having the formula:



which in an aqueous solution is of a pronounced soaplike character.

By using as original material the N-carbonyl-hexadecyl-sulphoacid-amide instead of the dodecylisocyanate there is likewise obtained a product having capillary active properties.

WINFRID HENTRICH.

HEINZ-JOACHIM ENGELBRECHT.

ERIK SCHIRM.

10 ccs of abs. alcohol containing about 20% of hydrochloric acid gas are added. One obtains a biscous crystal cake consisting of very fine crystals. It is heated, then cooled with ice-water and filtered, after standing, by suction. One obtains 9 grams of white Vitamin B₁ melting at 236° with decomposition.

3. To 16.2 grams of acetochloro-butyrolactone 1.8 ccs of water and 16-17 ccs of formic acid of about 100% are added and boiled for about 5 10 hours under reflux. Afterwards the formic acid is distilled off at reduced pressure and the dark coloured residue is distilled in vacuo at about 1.5 mm of Hg. One obtains 11-12 grams of 2-methyl-2-formyloxy-3-chloro - tetrahydrofurane which 15 contains 22% of chlor.

10-12 ccs of the above product are kept with 10

ccs of formic acid of about 90% and with 10 grams of 2-methyl-4-amino-5-(thioformamido-methyl)-pyrimidine for 40 hours at 50° in an incubator. The working-up of the reaction mixture can be carried out by methods given in the examples 1 or 2. One obtains 10.7 grams of Vitamin B₁ which is already in this state white and which melts at 236°.

The experimental conditions given in the foregoing examples can be varied in numerous ways. E. g. one may carry out the preparation of Vitamin B₁ at higher temperature, e. g. at 70°, but in this case the time of heating is to be reduced.

ZOLTÁN FÖLDI.
REZSŐ KÖNIG.

ALIEN PROPERTY CUSTODIAN

POLYESTERS

Paul Schlack, Berlin-Treptow, Germany; vested
in the Alien Property Custodian

No Drawing. Application filed June 12, 1941

The present invention relates to polyesters, and more particularly to polyesters containing amide groups.

It is known that highly polymerized products are in general readily obtained by condensing substances capable of forming linear polyamides in appropriate proportions, for instance, ω,ω' -diamines and ω,ω' -dicarboxylic acids and mixtures which contain functional derivatives thereof capable of forming polyamides in the presence of supplemental reactants (such derivatives are, for instance, esters, amides, nitriles, formyl compounds, urethanes, diamine salts of volatile acids, especially those of carbonic acid or formic acid, diisocyanates and compounds forming diisocyanates in the heat) instead of diamines or dicarboxylic acids or besides them, moreover ω' -aminocarboxylic acids and polyamide-forming functional derivatives thereof such as formyl compounds, urethanes, esters, amides lactams, nitriles (in the presence of water or water-forming substances) or mixtures of glycols and diisocyanates or substances forming such compounds. On the other hand one meets with considerable technical difficulties in producing highly polymerized polyesters, specially fiber-forming polyesters, so-called super-polyesters (confer G. V. Schulz, *Zeitschrift für physikalische Chemie*, 1938 A, volume 182, page 127) by simply condensing the reactants. The same is true in preparing polyesteramides containing in their molecule carboxylic acid ester groups as connecting links in addition to the amide groups. In these cases it is necessary to heat the reactants under a high vacuum for a very long duration (see, for instance, *Journal of American Chemical Society*, volume 54, pages 1557 et seq., 1566 et seq., and 1579 et seq.).

The present invention has as an object a process of easily preparing highly polymerized polyesters containing amide groups.

Further objects will be seen from the reading of the following description.

These objects are accomplished by first condensing reactants capable of forming polyesters, for instance, hydroxycarboxylic acids having at least five chain-forming atoms between the hydroxyl group and the carboxyl group, substantially equimolecular mixtures of glycols and dicarboxylic acids or aminoalcohols and dicarboxylic acids or mixtures of these compounds to form moderately highly polymerized polyesters or polyesteramides and then heating the obtained substances containing hydroxyl and/or carboxyl groups as reactive end groups with the

addition of a diisocyanate or a compound capable of splitting off a diisocyanate in the heat, until the desired high degree of polymerization is reached, the amount of the added diisocyanate being dependent on the number of the said end groups.

The diisocyanate may be added in one portion or by degrees, which latter step is more conveniently in most cases, for instance, by passing gaseous isocyanate into the liquid reaction mixture, if desired under pressure.

The following reactants can, for instance, be used for the production of the polyesters serving as the starting substance:

Hydroxycarboxylic acids such as 6-hydroxycaproic acid, 11-hydroxyhendecanoic acid, 12-hydroxystearic acid, ω -hydroxytetradecanoic acid, p-(ω -hydroxyethyl) benzoic acid.

Dicarboxylic acids such as carbonic acid, adipic acid, oxalic acid, succinic acid, maleic acid, glutaric acid, β -methyladipic acid, pimelic acid, sebacic acid, diglycolic acid, dipropylether- ω,ω' -dicarboxylic acid, dipropylsulfide- ω,ω' -dicarboxylic acid, phenylenedipropionic acid, isophthalic acid, 4,4'-diphenyloxidedicarboxylic acid.

Glycols such as ethyleneglycol, trimethyleneglycol, $\beta\beta'$ -dimethyltrimethyleneglycol, β -methyl- β -n-butyl-trimethyleneglycol, tetramethyleneglycol, hexamethyleneglycol, a mixture of glycols produced by reducing the esters from the acid mixture obtained by the oxidation of technical hexahydroresol, decamethyleneglycol, triethyleneglycol, thiodiglycol.

Aminoalcohols such as aminoethanol, 3-amino-1-propanol, 6-aminohexanol.

The polyesters used as the starting compound are prepared according to the usual methods (see *J. Am. Chem. Soc.*, volume 51, pages 2560 et seq., 2464 et seq., volume 52, page 314 et seq., and volume 55, page 4714).

The following diisocyanates and compounds splitting off diisocyanate on heating may, for instance, be employed for the reaction with the polyesters thus prepared:

Tetramethylenediisocyanate, pentamethylenediisocyanate, hexamethylenediisocyanate, octamethylenediisocyanate, decamethylenediisocyanate, m-phenylenediisocyanate, p-phenylenediisocyanate, 4,4'-diphenylenediisocyanate, diisocyanates from γ,γ' -diaminodipropylether, from ethyleneglycol-bis- ω -aminoethylether, from γ,γ' -diaminodipropylsulfide arylcarbamate ester from diamines such as hexamethylenediaminebenzidine, di- δ -aminobutylmethylaniline, the dicarbamic acid aryl ester from di- δ -aminobutylamine,

the addition products of diisocyanates as, for instance, hexamethylene-diisocyanate and compounds capable of being enolized such as acetic acid ester and dihydroresorcinol.

The process of this invention is not limited to starting substances which are only prepared by condensing compounds of the above-mentioned kind. Such mixed products are likewise useful as in addition to substances adapted to form polyesters contain in their molecule reactants forming polyamides on heating, for instance monoaminomonocarboxylic acids having at least five carbon atoms between the amino and carboxyl groups or combinations of diamines and dicarboxylic acids or are decomposed into three compounds on hydrolysis. Starting materials of this kind are, for instance products obtained by condensing any mixture of ϵ -aminocaproic acid or the lactam thereof and 11-hydroxyhendecanoic acid, the substance prepared by condensing 1 mol of hexamethylenediamine, 2 mols of adipic acid and 1 mol of tetramethyleneglycol, the mixed condensate produces from 1 mol of sebacic acid, 0.8 mol of tetramethylenediamine, and 0.2 mol decamethyleneglycol, and the mixed condensate prepared from 1 mol of adipic acid, 0.5 mol of ω,ω' -dihydroxy di-*n*-butylether, and 0.5 mol of hexamethylenediamine.

Moreover, products containing compounds having basic nitrogen atoms can be used, for example, polyamides containing *N*-methyldiethanolamine or *N*-di- ω,ω' -diaminodibutylamine (prepared from γ -bromobutylbenzamide and methylamine) as the component.

In addition to carboxylic acids linear polyurethanes may also be employed the chain ends of which are alcoholic hydroxyl groups. Such products are obtained according to a known process by reacting diisocyanates with glycols in excess, conveniently in the presence of a solvent.

The starting substances can be heated together with the diisocyanate or compounds forming diisocyanates on heating to form the products of the invention. It is, however, often of advantage to use solvents as, for instance, ethylene chloride, chlorobenzene, dioxane, diethylformamide, or pyridine, as the reaction can thus be carried out especially easily and uniformly. It is convenient to stir the mixture during the reaction in order to distribute the diisocyanate sufficiently. Instead of stirring a boiling solvent can be employed for mixing. It is not necessary that the process of the invention is carried out directly subsequent to the primary condensation; the after-condensation, if desired, for obtaining the superpolymeric condition can also be accomplished later and in another stage. The after-condensation can, for instance, be effected together with a procedure in which the mixture is molded into fibers, foils, coating layers, or shaped articles. Accordingly, the pre-condensate can be cautiously melted together with the necessary amount of diisocyanate and the obtained mass not readily condensed can lie stored until it is worked up, for example, into die cast articles. Hard powdered products pre-condensed can also be mixed with a powdered reactant as, for instance, hexamethylene-bis-2-hydroxydiphenylcarbamic acid ester (prepared by reacting the chloroformic acid ester of phenol with hexamethylenediamine or hexamethylene-diisocyanate with the corresponding phenol). The dry, if required, stored mixture is then heated to reaction temperature in the working up.

It is without difficulty to ascertain the amount

of diisocyanate or diisocyanate-forming substance necessary for preparing a polymer as highly polymerized as possible. It is merely necessary to vary the amount of the diisocyanate with respect to the starting material and ascertain the change in viscosity corresponding with the added amount. In order to regulate the relations of the reaction, it is also possible to determine the number of the reactive end groups (carboxyl and/or hydroxyl groups) with the acid of the hydroxyl and acid values or the movable hydrogen (Zerewitinoff) and calculate the amount to be added by means of the equivalent values found. If low-viscous products are required, the optimum amount of the substance to be added is to be reduced or increased as the case may be. The relations are most favorable if the two end groups are carboxyl. Therefore, starting substances are preferred which are prepared with an excess of the carboxyl reactant. It is, however evident that products can also be worked up which preferably have hydroxyl end groups. Such products are conveniently used if the formation of gaseous by-products, for instance, CO_2 is to be avoided, for example in after-condensing the reactants in conjunction with a spinning procedure or the like. For controlling the chain length monofunctional substances can be added in a manner known per se, especially compounds slightly volatile as, for instance, carboxylic acids such as stearic acid, *p*-chlorobenzoic acid, and benzaminocaproic acid, alcohols such as naphthylmethylalcohol, octadecylalcohol, and phthalylaminomethanol, or amines such as cyclohexylamine and octadecylamine.

The products highly polymerized of the invention can be worked up into fibers, foils and shaped articles in the same manner as the known highly polymerized polyesters and polyesteramides. They are especially suitable for preparing pliable foils and coatings for paper, fabrics etc. Some products of the invention are also valuable as sizing and finishing agents and the like.

The products of the invention cannot only be worked up into fibers and the like from the melt but in many cases from solutions thereof, for instance in esters, halogenated hydrocarbons or mixtures thereof with alcohols. Some products are also soluble in saturated or unsaturated alcohols and water, especially if the atom chains of the starting substances contain amide-, ether-, or sulfamide groups. The solubility is particularly increased of radicals of amino acids having a relatively short chain as, for instance, of ϵ -aminocaproic acid are present.

Polyesters having incorporated therein a sufficient number of basic amino groups by condensation are soluble in diluted acids such as acetic acid and can be applied from these solutions on fabrics, paper etc.

The more detailed practice of the invention is illustrated by the following examples. There are of course many forms of the invention other than these specific embodiments.

Example 1

A mixture of 1 mol of 9-aminononanoic acid, 1 mol of adipic acid, and 1 mol of decamethyleneglycol is heated at 225° C in an autoclave and an atmosphere of nitrogen for 4 hours. The water formed during the reaction is then cautiously blown off whereupon the mass is heated at 230° C in vacuo for 4 hours. The product obtained on cooling is waxy and hardly capable of being

drawn into useful fibers. A highly polymerized product adapted to form filaments from the melt is prepared by melting the mass with $\frac{1}{20}$ mol of octamethylenediisocyanate for each mol of bi-functional starting substance in the original mixture.

Example 2

A mixture of 1 mol of adipic acid and 1 mol of aminopropanol is heated in an autoclave from 150 to 200° C during 4 hours and kept at 200° C for 1 hour. After the formed water is blown off, the mass is heated at 220° C for 3 hours. $\frac{1}{30}$ mol of hexamethylenediisocyanate in the form of vapor is then passed into the melt whereupon the mixture is heated at 200° for a further hour. The product thus obtained can be worked up into fibers and foils.

Example 3

A completely dry polyurethane prepared by reacting 1 mol of 1,4-butyleneglycol with 0.95 mol of hexamethylenediisocyanate is mixed with 0.045 mol of octamethylenediisocyanate. The mass is then heated in fused condition for 1 hour. The polyurethane above-mentioned can also be mixed with an equivalent amount of diphenyl-4,4-diisocyanate whereupon the mass is melted together and subsequently molded. As the fused substance is low-viscous in the beginning, it can be worked up easily.

Example 4

A mixture of 11 mols of adipic acid and 10 mols of 1,4-butanediol is gradually heated to 180° C, the water splitted off being removed by distilling. After the pressure has been reduced to 10 mm/Hg, the temperature is raised to 200° C and the mass then heated at 200–210° C for 5 hours. On cooling the mass becomes hard and waxy (melting point 49° C, acid number 79). 40 parts (by weight) of this polyester are heated by degrees with 10.5 parts (by weight) of hexamethylene-bis-carbamic acid diphenyl-ester to 200° C whereby a great amount of CO₂ is splitted off, and maintained at this temperature for 1 hour. The phenol formed during this reaction is finally distilled off by heating the mixture in vacuo (water jet pump) at 200° C for 2½ hours. The light brown condensation product obtained on cooling is tenacious and elastic and soluble in methylenechloride, ethylenechlorohydrin and m-cresol. Melting point is 105° C; viscosity (sh/c) of a m-cresolic solution of 0.5 per cent strength is 0.63.

Example 5

A mixture of 10 mols of pentamethyleneglycol and 9 mols of adipic acid is condensed in boiling chlorobenzene until the splitting off of water is finished whereupon the solvent is distilled off and the mass is heated in vacuo at 180° C for 2 hours. The reaction product is then dissolved in methyl-

ene-chloride whereupon an equivalent amount of hexamethylenediisocyanate ascertained according to the method of Zerewitinoff and calculated from the number of the reactive hydrogen atoms is added. Sheets of paper are then impregnated with the solution thus obtained. A tenacious and homogenous impregnation is attained by subsequently heating the paper to 120° C.

Example 6

A mixture of 10 mols of adipic acid and 9 mols of pentamethyleneglycol is condensed in vacuo at 180° C until the splitting off of water is finished. The percentage of carboxyl groups is then determined by titrating a test portion dissolved in alcohol whereupon 1 mol of hexamethylenediisocyanate is added for two carboxyl groups. The mass is then after-condensed under normal pressure at 200–230° C until the viscosity does not increase any longer and the splitting off of CO₂ has ceased. The melt is especially suitable for forming filaments. With a glass rod filaments 10 m and more long can be drawn from the melt. The filaments are elastic like gum and can therefore be used as rubber substitute. They have the advantage over threads of rubber that they are resistant to aging. Foils produced from material after-condensed may be employed for the manufacture of protecting jackets and coverings.

The resistance to heat of the polymers can be increased by using suitable reactants as, for instance, fumaric acid, p-phenylenedipropionic acid, and high-melting glycols.

A specially elastic polymer is obtained by substituting β,β -dimethyltromethyleneglycol for pentamethyleneglycol.

Example 7

A mixture of 1 mol of maleic anhydride and 0.9 mol of 1,4-butanediol is heated to 180° C in an atmosphere of nitrogen and the presence of 0.18 gram of hydroquinone during 4 hours. After the pressure has been reduced to 10 m/Hg the temperature is kept additional 2 hours. The product obtained on cooling is yellowish white, soft and waxy. If this product is heated with 5.2% of its weight of hexamethylenediisocyanate from 100 to 180° C during 2 hours, a polymer is produced which is tenacious, foamy, rubber-like, soluble in warm ethylenechlorohydrin, and moldable by rolling.

If the mixture of the reactants is heated at 150° C instead of 180° in the first and second stage, a polymer more soluble than that above-mentioned is produced from the melt of which filaments elastic like rubber can be drawn. On heating in open air this polyester becomes insoluble in the solvents in the same manner as the known maleic acid polyesters.

PAUL SCHLACK.

ALIEN PROPERTY CUSTODIAN

DISSOLVING, SOFTENING, GELATINIZING
AND SWELLING AGENTS AND PLASTICAL
MATERIALS MADE THEREFROMWinfrid Hentrich and Rudolf Endres, Dessau-
Rossau, Germany; vested in the Alien Property
Custodian

No Drawing. Application filed June 14, 1941

This invention relates to compounds suitable for use as dissolving, softening, gelatinizing and swelling agents and to plastical materials made therefrom.

We have found that the carbonic acid esters of polyvalent alcohols comprising at least one thio-ether group in the molecule are excellent dissolving, softening, gelatinizing and swelling agents for all kinds of polymerisation products which are obtained by polymerisation of compounds comprising at least once the group



As compounds comprising at least once the group

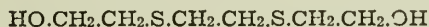


there may be mentioned for instance vinyl-alcohol, vinyl-ester, such as vinyl-chloride, wherein the polyvinyl-chloride may be subsequently halogenated after, vinyl-acetate, vinyl-chloracetate, vinyl-acetals, vinyl-alkyl ether, vinyl-thio-ether, vinyl-amines, vinyl-acetylene, divinyl-acetylene, vinyl-alkyl-ketones, acrylic acid, acrylic acid esters, methacrylic acid, methacrylic acid ester, vinyl-acetic acid, styrol, butadiene, isoprene, isobutylene and the like.

As dissolving, softening, gelatinizing and swelling agents for the polymerisation products of the aforementioned compounds according to our invention the carbonic acid esters of polyvalent alcohols are used in so far as these alcohols comprise at least one thio-ether group in the molecule. Such polyvalent alcohols are for instance thio-diglycol of the formula $\text{S}(\text{CH}_2\text{CH}_2\text{OH})_2$, γ, γ' -dioxy-propyl sulphide of the formula $\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_2$, bis-(β -oxypropyl)-sulphide of the formula $\text{S}(\text{CH}_2\text{CHOHCH}_3)_2$, β -oxyethyl- β' -oxypropyl sulphide of the formula



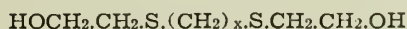
ethylene-bis- β -oxyethyl sulphide of the formula



tetraethylene-trisulphide glycol of the formula $\text{S}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2$ as well as compounds of the general formula $\text{S}(\text{CH}_2(\text{CH}_2)_x\text{CH}_2\text{OH})_2$ or



or



wherein x denotes a whole number between 1 and 10, and furthermore of the formula



For the esterification of the polyvalent alcohols having at least one thio-ether group in the molecule mainly aliphatic carbonic acids hav-

ing from 7 to 9 carbon atoms in the molecule and having a branched or unbranched chain come into question; these acids are obtained in the industry mainly as waste fatty acids.

Such carbonic acids are obtained, for instance, in the oxidation of paraffines. They are further contained in the acid by-products of the Fischer-Tropsch synthesis, in the lower fractions of natural fatty acid mixtures, for instance in the cocos-oil fatty acid, in the palm-kernel fatty acid and the like. Finally they may be obtained by dehydration of the high boiling alcohol fractions from the methanol synthesis. The esters of the polyvalent alcohols with at least one thio-ether group in the molecule with such aliphatic carbonic acids having from seven to nine carbon atoms in the molecule are of excellent value as regards their gelatinizing power and their electrical properties.

Furthermore, carbonic acids, such as acetic acid, lactic acid, butyric acid, capronic acid, caprylic acid and the like are suitable for esterifying the polyvalent alcohols having at least one thio-ether group in the molecule. For such purpose are furthermore suitable undecylenic acid, levulinic acid, butoxy-acetic acid, butoxy-ethoxy acetic acid, octyloxy-acetic acid, alkoxy-acetic acids in which the alkyl residue represents a hydrocarbon mixture having from seven to nine carbon atoms in the molecule, naphthenyloxy acetic acid, cresoxy acetic acid, phenyl acetic acid, benzoic acid, salicylic acid, benzoyl-benzoic acid. Of polybasic acids there may be mentioned succinic acid, adipinic acid, cyclohexane-diacetic acid and the like.

The production of the esters according to our invention is effected in the customary manner known as such and does not offer any technical difficulties.

The described softening agents and the like may easily be incorporated into the aforementioned products of polymerisation, especially into polyvinyl chloride which had not subsequently been chlorated. They are well compatible with other substances so that by simultaneously using these softening agents, from the products of polymerisation there may be made mixed products, for instance products mixed with cellulose derivatives, natural resins, natural caoutchouc, artificial albumene masses or other artificial resins. As compared with other esters which had so far been proposed for the same purposes the esters forming part of our present invention are advantageously distinguished by high gelatinizing power as well as by excellent electrical properties.

Example 1

25 parts by weight of polyvinyl chloride which had not been subsequently chlorated are kneaded together at about 160° with 75 parts by weight of

a thio-diglycol fatty acid ester having an acid component representing a fatty acid mixture with from seven to nine carbon atoms in the molecule, kneading being continued for such a length of time until a homogeneous mass has been obtained. This mass is thereupon rolled out into thin films by means of a calender, said films being excelled by high elasticity permitting to be worked into elastical coverings, such as protecting garments, protecting covers and the like.

Example 2

75 parts by weight of polyvinyl chloride are mixed with 25 parts by weight of a mixture of the fatty acid esters from thio-diglycol and waste

fatty acids having from seven to nine carbon atoms in the molecule and the mixture is rolled out in hot condition into a hide. A cable is covered with this homogeneous mass in known manner, thereby producing a cable covering of high elasticity, high resistance of cold and very high insulating power.

Instead of the mixture of the fatty acid esters from thiodiglycol and waste fatty acids having from seven to nine carbon atoms in the molecule there may also be used the dicapryl-acid ester of the ethylene-bis- β -oxyethyl sulphide.

WINFRID HENTRICH.
RUDOLF ENDRES

ALIEN PROPERTY CUSTODIAN

CAPILLARY ACTIVE AGENTS

Winfried Hentrich, Dessau - Rossau, Heinz-Joachim Engelbrecht and Erik Schirm, Dessau, Germany; vested in the Alien Property Custodian

No Drawing. Application filed June 14, 1941

This invention relates to capillary active agents and process of making same.

We have found that valuable capillary active agents may be produced by treating organic compounds which comprise in the molecule at least one sulphaamid group and at least an aliphatic residue comprising three or more carbon atoms with acylating agents.

When carried out this process, aliphatic, cyclo-aliphatic or aromatic sulphamides or mixed types of these series comprising at least an aliphatic residue having three or more carbon atoms may be used as original materials. The hydrocarbon residues of the sulphamides may also comprise oxygen, sulphur or nitrogen in the form of substituents or of hetero-atoms or groups of hetero-atoms. For instance, the hydrocarbon atoms may be interrupted by atoms of oxygen, sulphur or nitrogen and especially comprise CO.O , O.CO , NH_2 , CO.NH , NH.CO , SO_2 , SO.NH , NH.SO_2 , CO.NH.SO_2 , $\text{SO}_2.\text{NH.SO}_2$ groups.

As examples of such sulphamides may be mentioned: propyl-sulphamide, hexyl-sulphamide, isooctyl-sulphamide, dodecyl-sulphamide, hexadecyl-sulphamide, monochlorooctadecyl-sulphamide, octadecenyl-sulphamide, lauroyl-oxyethane-sulphamide, oleoyl-methyl-amino-ethane-sulphamide, γ -octyl-oxypropyl-sulphamide, 4-sec-butyl-cyclohexyl-sulphamide, diisobutyl-cyclohexyl-sulphamide, naphthenyl-sulphamide, isopropyl- or isobutyl-naphthalene-sulphamides, tetrahydronaphthalene- β -sulphamide, hexadecyl-benzol-sulphamide, 3-caproyl-amino-benzol-sulphamide, 3-n-octyl-sulphamino-4-chlorobenzol-sulphamide, 3-n-tetradecyl-urea-benzol-sulphamide, 3-hexadecyl-urethane-benzol-sulphamide, 3-diisobutyl-naphthyl-sulphamino-benzol-sulphamide and the like.

According to our present invention acylating agents are caused to act on these sulphamides or their salts, especially their alkali salts. Such acylating agents are carbonic acid halogenides, carbonic acid anhydrides, chlorated carbonic acid esters and chlorides of urea.

Suitable carbonic acid halogenides or anhydrides or anhydrides are for instance acetyl-chloride, acetic acid anhydride, phenoxy-acetyl-chloride, 4-isooctyl-phenoxy-acetyl chloride, butyric acid chloride, higher molecular fatty acid halogenides and their substitution products, pyromucic acid chloride, naphthenic acid chlorides, benzoyl chloride, benzoic acid anhydride, o-cresotic acid chloride, pyridine- or chinoline carbonic acid anhydrides, oxalyl chloride, succinic acid chloride, adipinic acid chloride, therephthalic acid

chloride, naphthalene-1,5-dicarboxylic acid chloride, thioglycolic acid chloride, diglycolic acid chloride, diglycolic acid anhydride, phthalic acid anhydride, isatoic acid anhydride and the like.

In a similar way also chlorocarbonic acid esters of aliphatic or cyclo-aliphatic hydroxyl compounds may be used, such as chlorocarbonic acid hexyl ester, chlorocarbonic acid dodecyl ester, chlorocarbonic acid methyl cyclohexyl ester and the like as well as urochlorides, such as for instance octyl urochloride, oleyl urochloride, benzyl urochloride, didodecyl urochlorides, dodecyl methyl urochloride and the like.

The hydrocarbon residues of the acylating agents pertaining to the aliphatic, cyclo-aliphatic or aromatic series or mixed types of these series may also comprise known hetero-atoms or groups of hetero-atoms, such as oxygen, sulphur, nitrogen, ester groups, carbonamide groups, sulphonamide groups and the like or substituents, such as halogen, hydroxyl groups, nitro groups and the like.

The reaction which is caused by the acylating agents takes place in accordance with methods that are known as such, eventually in the presence of indifferent organic solvents or, if salts of the sulphamides are used also in an aqueous medium. If necessary, the temperature may be increased to bring about the reaction and kept at 100° and higher to complete the reaction; furthermore there may be used as far as necessary agents able to bind acid or water. As solvents which at the same time act binding on acid, pyridine may for instance be used.

For the production of sulphamides which comprise carbonamide groups, such as for instance the 3-(capryloyl-amino)-benzol-sulphamide, the process may also be conducted in a modified way by using for instance the corresponding amino-alkyl- or amino-aryl sulphamides as original material and performing the acylation simultaneously on the amino group and on the amide group.

The capillary active agents produced by the process forming part of our present invention are of the general formula $\text{R.SO}_2.\text{NH.CO.R}'$. In this formula Ar denotes any desired organic residue consisting of an aliphatic residue comprising three or more carbon atoms or containing an aliphatic residue comprising three or more carbon atoms. The residue R, accordingly, may be of aliphatic, as well as of cyclo-aliphatic or aromatic nature, but must always comprise an aliphatic residue having three or more carbon atoms. The residue R may also comprise oxygen,

sulphur or nitrogen in the form of substituents or of hetero-atoms or groups of hetero-atoms. For instance, the hydrocarbons may be interrupted by atoms of oxygen, sulphur or nitrogen and may especially also comprise: CO.O, O.CO, NH₂, CO.NH, NH.CO, SO₂.NH, NH.SO₂, CO.NH.SO₂, SO₂.NH.SO₂ groups.

The residue R' denotes any desired organic residue, for instance an alkyl-, cycloalkyl-, aralkyl- or aryl-residue which may eventually be substituted. The residue R' may also comprise hetero-atoms or groups of hetero-atoms, such as oxygen, sulphur, nitrogen, ester groups, carbonamide groups, sulphonamide groups or substituents, such as for instance halogen hydroxyl groups, nitro groups and the like.

Compounds that may be obtained by the process forming part of our present invention are as follows: N-capronoyl-butyl-sulphamide, N-capronoyl-octyl-sulphamide, N-acetyl-lauryl-sulphamide, N-acetyl-diisobutyl-naphthalene-sulphamide, N-propionyl-oleoyl-methyl-amino-ethane-sulphamide, N-naphthenoyl-octadecenyl-sulphamide, N-(3-lauroyl-amino-benzol-sulphonyl)-benzamide, N-benzoyl-n-dodecane-sulphamide, mixtures of isomeric N-acetyl-diisobutyl-naphthalene-sulphamides, N-capryloyl-hexyl-sulphamide, N-caprinoyl-octyl-sulphamide, N-(3-capronoyl-amino-benzol-sulphonyl)-capronoyl-amide, N-(3-capryloyl-amino-benzol-sulphonyl)-capryloyl-amide, N-(3-caprinoyl-amino-benzol-sulphonyl)-caprinoyl-amide, and the like.

These compounds are possessed of surface active properties and show a considerable deterging, frothing, emulsifying and wetting ability, even if the hydrocarbon residues R or R' contained therein are relatively still low-molecular. It is emphasized that the optimum of the deterging property is present in such compounds in which the residues R or R and R' have about from 6 to 10 carbon atoms and are mainly of aliphatic nature. The compounds may advantageously be used for all deterging, cleaning, wetting, dispersing and emulsifying processes, such as are customary in the textile and washing industry, in the fur industry, in the leather industry and the like. The products may be used as such or also in combination with known washing and cleaning agents or additions to such agents.

Products of condensation have already been made by introducing higher molecular fatty acid residues into aromatic sulphamides, for instance into the p-toluol-sulphamide and it had been stated that these compounds are suitable for the making of washing agents. As compared with these known compounds the products of condensation obtained by the process forming part of our present invention are possessed of a better solubility in water and are of superior character as regards their surface active properties and especially as regards their washing properties. Above all, compounds with relatively low molecular fatty residues are likewise possessed of excellent washing properties.

Example 1

250 parts by weight of n-dodecane sulphamide and 145 parts by weight of benzoyl-chloride are heated to a temperature of 100° until the incipient lively development of hydrochloric acid ceases. Thereupon the temperature is slowly raised to 140° and the reaction mixture kept at this temperature, until hydrochloric acid will no more be given off. Now the mixture is coded and the solidified mass re-dissolved in 800 to 850 parts

by volume of benzene of a boiling point from 70 to 80°. There will be obtained about 290 parts by weight of N-benzoyl-n-dodecane-sulphamide (=82% according to the theory) in the form of a colorless crystalline powder with melting point at 77°. The powder dissolves clear in water by adding the necessary amount of soda, especially when applying heat; the solution is heavily frothing and possessed of a better washing property than a solution of N-lauroyl-benzol-sulphamide of the same concentration.

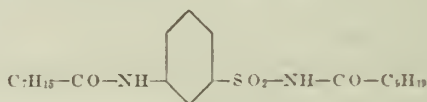
Example 2

34 parts by weight of the sodium compound of a technical diisobutyl-naphthalene-sulphamide mixture are suspended in 170 parts by weight of toluol. Thereupon 8 parts by weight of acetyl chloride are stirred into the mixture at ordinary temperature. The reaction mixture is heated, using reflux, to boiling temperature until the acetyl-chloride has been consumed. Now the toluol is blown off by water steam, the residual aqueous liquid, which should amount to about 500 parts by volume, is adjusted to be slightly basic, as indicated by the litmus test, filtered to remove small quantities of undissolved constituents, the filtrate strongly acidulated with hydrochloric acid and in order to complete the precipitation 125 parts by weight of common salt are added. The amorphous yellowish precipitate which is a mixture of isomeric N-acetyl-diisobutyl-naphthalene-sulphamides is filtered and dried. In a soda alkaline solution the product is an excellent wetting agent.

Instead of the acetyl chloride also acetic acid anhydride may be used. Similar substances are obtained, if monochloroacetyl-chloride, chloroacetic acid anhydride or chlorocarbonic acid-isobutyl ester is used instead of the acetyl chloride or acetic acid anhydride.

Example 3

3 parts by weight of 3-capryloyl-amino-benzol-sulphamide, 2 parts by weight of caprinic acid chloride and 10 parts by weight of xylol are heated to boiling temperature, using reflux, until the development of hydrochloric acid ceases. Thereupon the xylol is blown off with water with water steam or removed by distillation at considerably decreased pressure. The residual mass which consists mainly of a product of condensation of the formula:



easily dissolves in warm diluted soda solution, while heavily frothing.

In like manner for instance β-(oleoyl-methyl-amino-) ethane-sulphamide may be condensed with caprone-, capryl-, caprine-, laurin-, or oleic acid chloride.

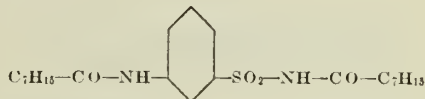
Example 4

5-stearoyl-amino-benzol-1,3-disulphamide is boiled, using reflux, with five times the amount of acetic acid anhydride, until acetylation is completed. Thereupon the formed acetic acid and the excessive acetic acid anhydride is removed by distillation, preferably at reduced pressure. The residue dissolves in a warm diluted soda solution, while heavily frothing, the same as the products according to the previous examples.

Example 5

86 parts by weight of metanil amide are dissolved in 1000 parts of water by adding 20 parts by weight of sodium hydroxide. A mixture of 180 parts by weight of caprylic acid chloride and 180 parts by volume of acetone is slowly stirred into the solution which had been cooled down to about 2°. During stirring the temperature is kept at 2 to 5° and, as soon as the alkaline reaction ceases, sodium lye is gradually added so that phenol-phthalein paper will steadily be colored slightly pink. Upon introduction of the caprylic acid chloride at freezing temperature there is observed no further conversion due to the mixture becoming neutral, the mass is gradually heated to 50° and eventually further amounts of sodium lye are added so that there is finally obtained a solution which remains permanently alkaline in warm

condition. The solution which may eventually be clarified by filtration is now acidulated with hydrochloric acid and the precipitate thus formed filtered and dried. Caprylic acid which may adhere to the solution may be removed by washing with benzine. The obtained product of condensation is of the formula:



This product dissolves on heating with diluted soda solution, while frothing.

WINFRID HENTRICH.
HEINZ-JOACHIM ENGELBRECHT.
ERIK SCHIRM.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PRODUCING CONDENSATION PRODUCTS

Winfried Hentrich, Dessau-Rosslau, and Wolfgang Gündel, Dessau, Germany; vested in the Alien Property Custodian

No Drawing. Application filed June 18, 1941

This present invention relates to condensation products and their production. More particularly it relates to the production of condensation products produced by reacting sulfinic acids with halogen hydrines and alkylene oxides.

Furthermore it relates to the production of esters of the condensation products with anorganic or organic acids.

It has been found that valuable condensation products are obtained by reacting halogen hydrines or alkylene oxides or halogen hydrines and alkylene oxides respectively upon sulfinic acids containing at least one aliphatic or alicyclic radical in the molecule or upon their salts respectively, and if necessary by esterifying the free hydroxyl groups present in the obtained condensation products with inorganic or organic acids.

Alkyl sulfinic acids which may be used as initial materials are e. g. ethyl, octyl, dodecyl, octadecyl sulfinic acid, a technical mixture of higher molecular alkyl sulfinic acids obtained by reduction of alkyl sulfonic acid chlorides produced from paraffin by reacting with chlorine and sulfur dioxide or from cyclohexyl, methylcyclohexyl and isooctylcyclohexyl sulfinic acid, further from tetrahydromenaphthyl sulfinic acid, n-octylbenzol sulfinic acid, isobutyl-naphthyl sulfinic acid, isopropyltetrahydronaphthyl sulfinic acid, cresoxybenzol sulfinic acid and the like. The hydrocarbon radicals of the sulfinic acids may also contain oxygen, sulfur, nitrogen or halogen in substituents or in hetero atoms or hetero groups, which are introduced.

The production of the sulfinic acids is known. They are obtained e. g. by treating sulfonic acid halogenides with reducing agents such as zinc, further by reacting sulfur dioxide with the corresponding hydrocarbons in the presence of aluminium chloride or, in the aromatic series, by acting alkali sulfide solutions upon aromatic sulfo chlorides in the warmth.

According to this invention upon the sulfinic acids or their salts such as alkali salts halogen hydrines or alkylene oxides or halogen hydrines and alkylene oxides respectively are allowed to react. As halogen hydrines are used for this process e. g. ethylene chlorhydrine, glycerine- α -monochlorhydrine, β -chloro- β' -hydroxydiethyl-ether, pentaethylene glycolchlorhydrine and higher molecular chloro- or bromo-hydrines. The reaction is preferably performed upon salts of the sulfinic acids or, respectively, in the presence of acid-binding agents. Solvents or diluents may be employed, as well as pressure and advantageously increased temperatures. The working

up of the condensation products is done in the usual manner. Then the thus formed condensation products containing hydroxyl groups in the molecule may be treated with alkylene oxides.

Alkylene oxides which may be applied for the reaction upon sulfinic acids or their salts as well as upon the aforesaid condensation products with halogen hydrines may be e. g. the ethylene oxide, further 1,2-propylene oxide, 1,2-butylene oxide, glycid, epichlorhydrine, cyclohexene oxide and the like. The reaction of the ethylene oxide is preferably performed in the presence of catalysts e. g. potassium ethylate and under pressure as well as at increased temperatures either with or without applying any solvents or diluents. The addition may be made in such a manner as to obtain products containing in the molecule one or more hydroxy-alkyl radicals. The condensation products having more than one hydroxy-alkyl radical may be watersoluble products whereat the more ether radicals are to introduce the higher molecular are the hydrocarbon radicals of the sulfinic acids.

For a further enhancement of the water solubility the free hydroxyl groups of the obtained condensation products if necessary may be esterified with poly basic inorganic or organic acids e. g. with sulfuric acid, phosphoric acid, succinic acid, adipic acid, phthalic acid and the like.

According to the present process the following compounds may be obtained: butyl-(β -hydroxyethyl)-sulfone, the sulfuric acid ester of the octyl-(β -hydroxyethyl)-sulfone, dodecyl - (β, γ - dihydroxypropyl)-sulfone, methyl-cyclohexyl-(β -hydroxypropyl)-sulfone, n-octylbenzol-(β -hydroxyethyl)-sulfone, the addition product of 8 mols of ethylene oxide to a technical mixture from hexadecyl- and octadecyl-sulfinic acid, the addition product of 12 mols of ethylene oxide to montanyl sulfinic acid etc.

Those condensation products are of a particular technical interest, if they are watersoluble and derived from higher molecular sulfinic acids containing at least one lipophile group that is a higher molecular aliphatic or cycloaliphatic radical of at least six carbon atoms or a cycloaliphatic or aromatic radical having an aliphatic side chain of at least four carbon atoms in the molecule. In this case they represent products having wetting-, emulsifying-, washing- and deterging-properties and may advantageously be applied as soap substituents in the leather, fur and textile industry and especially in laundries. But the low molecular and not watersoluble condensation products are likewise of a technical

interest by being applicable as softening and plastifying agents for cellulose derivatives, artificial stuffs e. g. of the poly vinyl series, natural or artificial caoutchouc and the like.

In the further development of the above described process it has been found that technically valuable materials are obtained by introducing hydroxyether or hydroxypolyether radicals into nonsubstituted or nonaliphatically or noncycloaliphatically substituted aromatic sulfinic acids by a treatment with halogen hydrines or 1,2-alkylene oxides or halogen hydrines and 1,2-alkylene oxides respectively.

In performing this process as initial materials e. g. benzene sulfinic acid, benzene-1,3-disulfinic acid, naphthalene sulfinic acids, naphthalene-1,5-disulfinic acid, naphthalene-1,3,5-trisulfinic acid, diphenyl sulfinic acids, anthracene, pyrene, chrysene, phenanthrene, anthraquinone sulfinic acids and other monobasic and polybasic sulfinic acids may be used which may also contain one or more substituents such as halogen atoms, nitro groups, acylamino groups, azo groups, alkoxy, aryloxy groups, trifluormethyl groups, alkyl or arylsulfone groups, alkyl or aryl mercapto groups, further OH—, HS—, H₂N—, COOH-groups and the like. Such compounds are e. g. 4-chlorobenzene sulfinic acid, 3,4-dichlorobenzene sulfinic acid, 2,5-dibromobenzene sulfinic acid, 3-nitrobenzene sulfinic acid, 3-nitro-4-chlorobenzene sulfinic acid, 5-nitro-2-bromobenzene sulfinic acid, 4-acetylaminobenzene sulfinic acid, 4-methoxybenzene sulfinic acid, 4-phenoxybenzene sulfinic acid, trifluormethylbenzene-3-sulfinic acid, diphenyl-sulfone-3-sulfinic acid, benzophenone-3-sulfinic acid, phenyl-n-butyl-sulfone-3-sulfinic acid, 2-chlorophenol-4,6-disulfinic acid, 1-amino-2,5-dichlorobenzene-4-sulfinic acid, 1-hydroxy-2-carboxy-benzene-4-sulfinic acid, 1-chloro- or 1-methyl-benzene-2,4-disulfinic acid, benzene-1-sulfinic acid-4-sulfonic acid, benzene-1-sulfinic acid-3-carboxylic acid, naphthalene-2-sulfinic acid-4,8-disulfinic acid and the like. Moreover the aromatic rings may also be condensed with heterocyclic ring systems e. g. in the quinoline-Bz-sulfinic acids or in carbazol- or diphenylene-oxide-mono- or poly-sulfinic acids respectively.

The manufacture of these sulfinic acids or their salts respectively is known. It is performed e.g. by treating the corresponding sulfonic acid halogenides with reducing agents such as zinc, or by the reaction of alkali sulfite solutions upon the sulfonic acid chlorides in the warmth, or from aromatic diazonium compounds and sulfur dioxide in the presence of copper powder or from sulfur dioxide and aromatic hydrocarbons in the presence of Friedel-Craft's catalysts.

Upon the sulfinic acids or their soluble salts e.g. alkali salts according to the present invention halogen hydrines or 1,2-alkylene oxides or halogen hydrines and 1,2-alkylene oxides respectively are allowed to react.

One may use as halogen hydrines—as indicated above—e.g. ethylene chlorhydrine, glycerine- α -mono-chlorhydrine, β -chloro- β' -hydroxydiethyl-ether, pentaethyleneglycol chlorhydrine and other chloro- or bromohydrines or, respectively, halogen compounds of other ether-alcohols.

The condensation reaction is performed as described above. The working-up of the condensation products is carried out in the usual manner.

The thus formed condensation products having hydroxy groups in the molecule may further be treated with 1,2-alkylene oxides or halogen hy-

drines. This treatment is applied especially if by the conversion with the halogen hydrines only one alkyleneoxy radical has been introduced into the molecule, as it occurs e. g. in converting with ethylene chlorhydrine.

Thus one may produce the β -phenyl-sulfone-ethylalcohol from benzene sulfinic acid sodium and ethylene chlorhydrine and treat this compound with one or more mols of 1,2-alkylene oxides or, respectively, react in the form of the sodium compound of the phenyl-sulfone-ethylalcohol with halogen hydrines such as ethylene chlorhydrine or, respectively, with the chlorhydrines of other polyvalent alcohols, especially of halogen hydrines of the poly glycols.

Furthermore the 1,2-alkylene oxides may be allowed to react upon halogen hydrines and the reaction products may be converted with the sulfinic acids.

The free hydroxy groups of the obtained addition products may be esterified, as described above, with monobasic or polybasic inorganic or organic acids.

The hydroxyether or hydroxypolyether sulfones obtained in this way such as phenyl- β -hydroxyethoxyethyl sulfone, 3,4-dichloro-phenyl- β -hydroxyethoxy-hydroxyethoxy-ethyl sulfone, the addition product of 3 mols of ethylene oxide to 3-nitrobenzene sulfinic acid, of 4 mols of ethylene oxideto xenyl-4-sulfinic acid, or 12 mols of ethylene oxide to naphthalene- α -sulfinic acid, of 6 mols of ethylene oxide to the benzene-1,3-disulfinic acid and the like have the properties of disagents for the manufacture of films, foils, plastic masses or artificial masses from gelatine, albuminous artificial masses, cellulose ethers, cellulose esters with low molecular fatty acids etc. They may also be applied as novel intermediate products for the synthesis of dyestuffs and remedies.

Example 1

203 parts by weight of a mixture of higher molecular alkyl sulfonic acid chlorides as obtained by the simultaneous reaction of chlorine and sulfur dioxide upon a paraffin fraction according to Fischer-Tropsch from boiling point 200 to 320° C. are dropped into a boiling mixture of 176 parts by weight of zinc powder and 700 parts by weight of water. After the addition is finished one continues boiling for a little while. After cooling it is filtered by means of suction and the filter cake which contains besides zinc oxide the zinc salt of the sulfinic acid, is stirred into a solution of 176 parts by weight of soda in 900 parts by weight of water. The mixture is heated up to boiling and filtered. From the soda alkaline solution by a careful acidifying with diluted sulfuric acid the free sulfinic acids are obtained, which are separated off and dissolved in an equivalent amount of a 4% soda lye. If necessary the slightly alkaline solution is filtered and then treated in the autoclave at 100 to 200° C with 400 parts by weight of ethylene oxide. After cooling the reaction mixture is neutralised with sulfuric acid and evaporated to dryness. To eliminate the inorganic impurities the residue is dissolved in alcohol, the solution is filtered, if necessary under addition of animal charcoal, and then the solvent is distilled off again. It remains a mass thickly liquid in the cold and soluble in water. The aqueous solution of the product possesses soap-like properties.

Example 2

27.4 parts by weight of crystallised dodecane

sulfinic acid sodium together with 8 parts by weight of ethylene chlorhydrine dissolved in 350 parts by weight of alcohol are heated under reflux up to boiling till the reaction is accomplished. After separating off the sodium chloride formed the alcohol is distilled off finally in applying reduced pressure. The residue is dissolved in 150 parts by weight of xylol and after an addition of 0.2 parts by weight of potassium ethylate is treated in the autoclave at 140° C with 35.2 parts by weight of ethylene oxide. After expelling the solvent there remains while cooling a waxlike solidifying mass soluble in water and having soaplike properties.

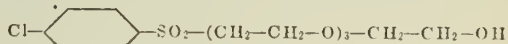
Example 3

200 parts by weight of crystallised benzene sulfinic acid sodium are dissolved in 800 parts by weight of water and converted in a stirring autoclave at 50–60° C with 220 parts by weight of ethylene oxide, whereat the introduction of the ethylene oxide is preferably done in portions. When the addition which begins rapidly is finished the mixture is warmed up for a little while to 90°. The reaction mixture now alkaline is strictly neutralised by an addition of hydrochloric acid. Then the water is distilled off under reduced pressure. To eliminate the sodium chloride formed the residue is dissolved in alcohol and filtered if necessary under addition of animal charcoal. After evaporating the alcohol a clear oil easily soluble in water is obtained the sulfur and hydroxyl contents of which points to a condensation product of the average composition corresponding to the formula



Example 4

230 parts by weight of crystallised p-chlorobenzene sulfinic acid sodium are converted with 100 parts by weight of ethylene chlorhydrine in a shown manner. 110 parts by weight of the p-chlorophenyl- β -hydroxyethyl sulfone obtained by the conversion are dissolved in 500 parts by weight of xylol and treated with 140 parts by weight of ethylene oxide in the stirring autoclave after addition of 1 part by weight of potassium ethylate at 110 to 120° C. After finishing the reaction and working-up a thickly liquid oil easily soluble in water is obtained the characterising numbers of which point to a product of the average composition corresponding to the formula



Example 5

40 parts by weight of ethylene chlorhydrine are dissolved in 120 parts by weight of water and are converted after addition of 1 part by weight of an 8% soda lye with 90 parts by weight of ethylene oxide at 110° C in the stirring autoclave. When the reaction is accomplished to the mixture 127 parts by weight of crystallised 3-nitrobenzene-sulfinic acid sodium are added and then the mixture is heated up for several hours under reflux until boiling. To isolate the formed polyoxethyl-3-nitrophenyl-sulfone the water is distilled off under reduced pressure, the residue is dissolved in alcohol, the separated sodium chloride is filtered off and the alcohol is distilled off again. After drying in the vacuo a dark-yellow oil remains which is easily soluble in water.

WINFRID HENTRICH.
WOLFGANG GÜNDEL.

ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCTS AND PROCESS FOR MAKING THEM

Erik Schirm, Dessau, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed June 19, 1941

This invention relates to products of condensation to be used as tannins and process of making said products.

I have found that technically valuable products of condensation may be obtained if sulfite waste liquor is condensed with aromatic sulfamides and aldehydes, especially formaldehyde or substances giving off formaldehyde. By this process the tanning properties of the sulfite waste liquor are improved to such an extent that the products of condensation will form valuable tannins, while the sulfite waste liquor itself, as known, can only be regarded as auxiliary tannin.

By the term "sulfite waste liquor" there should be understood the waste liquor obtained when disintegrating wood according to the sulfite process and the like, or the concentrates or dry substances that are obtained by evaporation and preferably freed from iron and lime.

Aromatic sulfamides or their nucleus substitution products which come into consideration as initial materials for the present process are for instance: benzene sulfamide, 4-toluol sulfamide, 4-chlorobenzene sulfamide, benzene-1,3-disulfamide, diphenyl-4,4'-disulfamide, naphthalene-1,3,5-trisulfamide, carbazol-tetrasulfamide, benzoic acid-3-sulfamide, 2-oxy-benzoic acid-5-sulfamide, benzoic acid-3,5-disulfamide, phenol-2,4,6-trisulfamide, 1-oxy-naphthalene-8-sulfamide, 1-oxy-naphthalene-8-sulfamide-3-sulfo-acid and so forth. For the present process are furthermore suitable the sulfamides which are obtained by the action of ammonia onto the resinous sulfochlorides obtained by sulfonation, for instance, with chlorosulfonic acid, of cyclic compounds of the aromatic type, for instance, of benzene, naphthalene or their nucleus substitution products or of carbazol, pyridine, thiophene and the like in presence of tetrachloride of carbon. These resinous products comprise sulfochloride groups and are of viscous constituency in heated condition, while being of hard constituency and of brown color in cold condition.

The hydrocarbon radicals of the sulfamides may comprise quite generally substituents, such as methyl-, ethyl-, hydroxyl-groups, halogen and the like or also hetero-atoms and heteroatom-groups, such as for instance ether-, sulfone-, ester-, sulfonamide-, carbonamide-groups and so forth.

As aldehyde components for the present process mainly formaldehyde, acetaldehyde, glyoxyl, acrolein, croton-aldehyde, furfural etc. or also corresponding compounds giving off aldehyde come into consideration, such as para-formalde-

hyde, trioxy-methylene, formaldehyde-bisulfite, methylal, hexa-methylene-tetramine etc.

The process may also be conducted in such a manner that first preliminary condensation products are formed from the sulfamides and the aldehydes and that thereupon these products are caused to act onto the sulfite waste liquor. As known condensation products of this kind there may be mentioned the N-methylol compounds of the sulfamides and their halogen-hydracid esters, that are the N-halogen-methyl compounds of the sulfamides, which compounds may be obtained in known manner by action of the aldehydes onto the sulfamides, eventually by the use of proper amounts of hydrochloric-acid.

The conversion between the initial materials and the sulfite waste liquor takes place in an aqueous medium by heating to temperatures of about 100°. The conversion is completed as soon as the condensation product is soluble clear in water.

Example 1

640 parts by weight of sulfite waste liquor freed from iron and lime and treated by evaporation as far as to powdrous constituency with a dry content of 93.6% are stirred together with 360 parts by volume of water, until a homogeneous syrup is formed. Now 250 parts by weight of N-methylol-p-toluol sulfamide are added and the mixture, after having become homogeneous by stirring, is heated to 90° and stirred at this temperature, until a sample of this mass is soluble clear in much cold water. After dilution with water and adjustment of the suitable pH value the product is ready for use as a tannin.

Example 2

426 parts by weight of a finely powdered technical mixture of benzene-1,3-disulfamide and benzene-1,4-disulfamide, such as is obtained by energetic sulfonation of benzene with excessive chlorosulfonic acid and conversion of the isolated mixture of benzene-1,3-disulfochloride and benzene-1,4-disulfochloride with ammonia are added to the syrupy sulfite waste liquid obtained according to Example 1 and the mixture well stirred. Thereupon 170 parts by weight of a solution of 40% aqueous formaldehyde are stirred into this mass at a temperature between 20 and 25° within a time amounting to two hours, stirring being continued at ordinary temperature for about 5 hours. Now the mass is heated to a temperature between 90 and 100° and this temperature maintained for about three hours, whereupon a sample of the mass shall be soluble clear in water.

If this is the case, the reaction mixture is evaporated to dryness at reduced pressure and at the temperature of the water bath. The residue which is obtained yields 888 parts by weight and may easily be ground, whereupon it will form a brownish gray powder which is readily soluble in water. The product is an excellent tanning agent.

In the aforegiven Example the benzene disulfamide may be replaced by 250-300 parts by weight of naphthalene-1,3,5-trisulfamide or naphthalene-1,3,6-trisulfamide or by the same amount of a technical mixture of isomeric naphthalene-trisulfamides. With the same mode of working a product is obtained which is similar to the afore described product.

Example 3

The benzene disulfamide according to Example 2 is replaced by 266 parts by weight of a sulfamide having a nitrogen content of 10.5%, which sulfamide had been made by action of concentrated ammonia water from a resinous sulfochloride obtained from naphthalene. The mode of working is in other respects the same as according to Example 2. In this case also there will be obtained a powderous tannin which is easily soluble in water.

ERIK SCHIRM.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF PRODUCTS OBTAINED FROM SUPERPOLYAMIDES

Franz Emich, Heppenheim, Germany; vested in the Alien Property Custodian

No Drawing. Application filed June 30, 1941

The present invention concerns a process for the production of products obtained from superpolyamides.

It is known that superpolyamides are suitable for the production of a great variety of shaped products, as for example films, artificial threads and such like. Superpolyamides represent high molecular, polypeptide-like condensation products of for example ω - ω -diamines and ω - ω -dicarbonic acids or ω -aminocarbonic acids or mixtures of these.

The superpolyamides known in the trade represent grains or lamellas containing about 7% of water. Pulverized superpolyamides have not yet been heard of, which fact probably is due to their extraordinary elasticity. It turned out to be exceedingly difficult to pulverize them by help of the usual methods.

The superpolyamides obtainable in commerce are worked up according to the following method: The lamellas are heated to melting temperature whereupon the melt, for example by die casting or press casting is given the desired shape. The production of a homogenous melt is very difficult. One nuisance consists in a formation of gas taking place. In the case of slight overheating considerable decompositions are observed which cause discoloration. In many cases the shaped products prepared from the melt have a porous surface and contain cavities. These impurities contained in the products known in the trade are transferred to the products with which they are to be worked up.

Thorough experiments have shown that working up of superpolyamides in order to obtain various products may be improved in every respect by admixing more water than is usually contained in air-dried superpolyamides. The superpolyamides usually contain about 7% of water. According to my invention objects, such as shaped products, powder and such like are produced from superpolyamides by first converting them into intermediate products rich in water, such as melts or pastes, whereupon these are subjected to a subsequent treatment. The water may be incorporated by heating the superpolyamides to suitable temperatures in the presence of water, preferably under water. The process is performed under pressure. In carrying out this process according to my invention I proceed as follows: The superpolyamides obtainable in the trade in lamella-form or perhaps in larger pieces are heated in pressure-vessels under water to melting temperatures or temperatures, which are lying above the melting point of the initial products.

Of course such temperatures are to be avoided which will cause damages, for example decompositions. I may, however, proceed in such manner that the superpolyamides are heated to only lower temperatures, which will just suffice for softening the superpolyamides and enable them to absorb water. This heating process is continued with until all of the desired amount of water is homogenously taken up by the superpolyamides. According to the kind of superpolyamide employed, the temperatures and the duration of heating smaller or larger amounts of water may be incorporated with the superpolyamide, whereby the qualities of the melts or of the products prepared from the melts resp. may be influenced more or less. The heating of the superpolyamide may, for example, be interrupted after the softening of the melts has taken place, whereupon the heating may be carried on with for a shorter or longer time, in order to cause the superpolyamide to go on absorbing as much water as is desired.

It became evident that during the working process by which shaped products are to be obtained, the increase in the amount of water contained in the air-dry starting material is of great advantage. This content of water, which amounts to 7%, may be increased by a few percent only, for example 2-4%. With some starting materials the best results were obtained, if the increase in water amounted to 4-6%. For the preparation of powdery products it has proved to be advantageous to introduce considerably larger quantities of water into the intermediate products. Heating of the initial products under water according to the present invention is advantageous insofar as impurities of the starting products will be taken up by the water. Consequently purer final products are obtained. In some cases it has proved to be useful to add to the water as well other products, which may be mixed with water, such as glycerine and/or glycol.

The melts or pastes according to the invention to which water has been added, may be worked up in various manners. They may, for example, be shaped by casting, die casting or press casting. Another method consists in converting the melt to which water has been added, first, by lowering of the temperature, into a plastic kneadable mass, whereupon this mass is further worked up, for example by giving it shape and drying it. Another method consists in converting the intermediate products, to which water has been added, into powdery superpolyamides, which again may be worked up,

Examples

1. $\frac{1}{2}$ kg. of superpolyamide of adipic acid hexamethylene-diamine and ω -aminocaproic acid of melting point 180° C. containing 7% of water, is heated to melting in a pressure vessel, the capacity of which amounts to about 4.5 liter, and which contains 2 liter of water. The necessary temperature of about 180° C. being reached the amount of water contained in the melt has gone up to 12%. The melt's consistency corresponds to, say, that of thin honey. This melt may preferably be used for the production of shaped products, for example for casting in molds, die casting, press casting or other means. Generally the working process should be proceeded with before any disturbing cooling down, for example to temperatures below 100° C. has taken place.

When cooling down to temperatures of about 50° C. or less the melt is getting plastic and rather viscous and may then be shaped. This shaping of the mass may be carried out according to usual methods. Products of any desired shape may be obtained. For example films may be prepared from the melt as well as the plastic mass, for example in such manner that first a rather thick film is prepared, whereupon this is treated between rollers or with other means until the desired thickness is obtained. I have found that the products prepared from the melt or the plastic mass practically did not show any disturbing shrinkage. The strength of the shaped products may be considerably increased by suitable after-treatment, for example by putting them into water of suitable temperature, for example of about 60° C.

Pasty intermediate products with an increased content of water may advantageously be worked up in such manner that they are kneaded or treated between rollers together with other substances, such as artificial substances, for example artificial rubber, based on butadiene, filling material, as for example carbon black. If desired several substances of various kind may be employed.

According to one embodiment of the invention the contents of the pressure vessel, after having been heated to its melting temperature of about 180° C. is kept on heating, whereby the same temperature is maintained. This method allows more water to be introduced. After about $2\frac{1}{2}$ hours' heating the content of water of the now thinly liquid melt amounts to 33%. During cooling down this melt rich in water is turning into a moist product, which essentially consists of powdery particles which are sticking together. These may exceptionally easily be converted into powder by means such as crushing, pulverizing or grinding. If the mass is cooling down in a pressure vessel under water while it is being stirred a powdery product may be obtained immediately.

The obtained moist powder loses the superfluous water very easily. It may be converted

into a superpolyamide containing the normal amount of water, of for example about 7%, by keeping it at the air or by drying it at moderate temperatures, for example such below 60° C., if desired in vacuo. The physical qualities of the powdery products may be influenced by variation of the process as described as above with respect to temperature, duration of heating and amount of water to be introduced. The obtained powders are much better suited for various purposes than the lamella-formed or granulated products as are obtained in the trade. The powder may, for example, directly be shaped by only applying heat and pressure, if desired together with other substances. Further on it is much easier to convert powder into homogenous melts than lamellas or the like.

The moist powder, which is obtained at first, may advantageously be made use of as well. For example I found out that this powder may easily be worked up together with admixtures, for example artificial substances or filling material, as for example carbon black, zinc white or the like, or with a plurality of substances, for example artificial rubber based on butadiene, and filling material, by kneading, treating between rollers or the like, whereby homogenous products are obtained, which have excellent qualities.

During the production of such mixed products the quantitative relation may range in between wide limits. One may, for example, prepare products of artificial rubber, based on butadiene and superpolyamides, which obtain up to 90% and, if desired, even more superpolyamides, and which as well contain filling material of the usual kind. The amount of filling material may be varied as much as is wanted.

2. $\frac{1}{2}$ kg. of a superpolyamide of adipic acid hexamethylene-diamine is heated to melting temperature, i. e. in this case to 250° C., in a pressure vessel under water under conditions as described in Example 1. When having reached melting temperature the melt, which is somewhat more viscous than the melt according to Example 1, contains about $12\frac{1}{2}\%$ of water. The melt may be worked up according to Example 1 in order to obtain shaped products and the like. If the contents of the autoclave is kept on the same temperature of 250° C. the melt may take up larger quantities of water. After about 3 hours' heating the content of water of the melt amounts to 100%. The melt rich in water may, according to Example 1, be worked up in such manner that powdery products are obtained.

3. $\frac{1}{2}$ kg. of the superpolyamide according to Example 2 is heated in a pressure vessel until it is soft and represents a viscous paste. After the paste is taken out of the pressure vessel it is immediately pressed into a mold, for example a wooden mold, whereby the product takes on the desired shape.

FRANZ EMICH.

ALIEN PROPERTY CUSTODIAN

PREPARATION OF HIGH MOLECULAR CELLULOSE DERIVATIVES

Siegfried Petersen, Leverkusen-Schlebusch II,
and Karl Taube, Leverkusen-I. G. Werk, Ger-
many; vested in the Alien Property Custodian

No Drawing. Application filed July 1, 1941

The present invention relates to the prepara-
tion of high molecular cellulose derivatives and to
the new products which are obtainable thereby.

In accordance with a known process halogen-
ides of di- or polybasic acids are caused to react
upon such cellulose derivatives as still contain free
hydroxy groups. The said process results in the
forming of a net work between the cellulose mole-
cules. In consequence thereof, the cellulose de-
rivatives become insoluble in organic solvents or
at least only capable of being swollen thereby.
The said prior known process is accompanied by
the disadvantage that during reaction free hy-
drogen chloride is evolved which may have a
breaking-down effect upon the cellulose deriva-
tives. Moreover, in practice the prior known
process can be performed only by contacting the
ready made shaped articles from such cellulose
derivatives either with a solution or with a vapor
of carboxylic acid halogenides of the character
described. If one would try to dissolve these
starting materials in a common solvent they
would enter into reaction spontaneously and
the reaction product would be precipitated as an
insoluble mass which is no longer capable of be-
ing molded or only with difficulty.

It is the object of our present invention to
obviate these difficulties and to develop a new
process which allows one to convert such cellulose
derivatives into a higher molecular state, thus
improving their stability towards heat and to-
wards organic solvents, without affecting their ca-
pability of being molded. Other objects will be
apparent from the following description and
claims.

In accordance with our present invention esters,
ortho-esters or acetals which contain several
functional groups which are capable of undergo-
ing a re-esterification or a re-acetalisation reac-
tion at a temperature up to about 220° are caused
to react at a higher temperature upon cellulose
derivatives of the character described. The heat-
ing of such starting materials with each other
results in the formation of a net work between
the cellulose derivatives, alcohols, phenols and so
on being split off from the said esters, ortho-
esters or acetals and replaced by the cellulose de-
rivatives. The re-esterification and re-acetalisa-
tion reactions described occur only at a higher
temperature, so that mixtures containing both
types of starting materials can be stored, worked
and molded in the usual manner. Thus, lacquer
solutions can be built up from starting materials
of the character described, if desired, with the
addition of softeners, pigments and dyestuffs.

Lacquer solutions of the character described can
be applied onto any desired surface and, after
drying, baked by exposing the coatings to a tem-
perature of above about 150° C. The coatings
thus obtained are characterized by their excel-
lent stability towards organic solvents. Further-
more, solutions containing cellulose derivatives
of the character described and esters, ortho-
esters or acetals of the type referred to above can
be employed for preparing threads, foils or
bristles according to a dry or wet spinning pro-
cess, which after having been exposed to a tem-
perature of say above about 150° C show an im-
proved stability towards solvents and heat.
Finally, our new process can be made use of in
the preparation of heat-hardening materials
which can be employed for the making of molded
articles.

As cellulose derivatives which can be employed
for the process of our present invention there may
be employed partly alkylated, aralkylated or
acylated cellulose derivatives such as cellulose,
benzylcellulose, cellulose acetate, cellulose pro-
pionate and mixed esters such as aceto butyrate.
Suitable esters and ortho-esters and acetals of
the character described are sulfurous acid-bis-
phenyl ester, oxalic acid-bisphenylester, formic
acid-ortho-ethylester, succinic acid-ortho-ethyl-
ester, formaldehyde-dibutylacetal, formaldehyde-
di(β -chloroethyl)-acetal and acetone-dibutyl-
acetal.

The following examples illustrate the invention
without restricting it thereto, the parts being by
weight:

Example 1

6 parts of acetylcellulose (54% of acetyl) are
dissolved in 24 parts of acetone, 12 parts of toluene
and 18 parts of glykolmonomethyletheracetate.
1 part of sulfurous acid-bisphenylester (see "Lie-
bigs Annalen" vol. 485, page 274, 1931) being dis-
solved in some acetone is added to the solution.
The solution thus prepared is applied or sprayed
onto a support; after drying the coating is baked
by a short heating to 180-190°C. There is ob-
tained an adhesive coating which is insoluble in
acetone.

Example 2

2 parts of oxalic acid-bis-phenylester being dis-
solved in a mixture of 4 parts of alcohol and 4
parts of glykolmono-methyl-etheracetate is mixed
with a solution of 10 parts of acetyl-cellulose of
the composition as described in example 1. The
clear lacquer obtained is applied onto a support
and, after drying, baked by a short heating to

temperatures of about 180–200° C. It is insoluble in organic solvents and shows a good adhesion on its support.

The acetylcellulose can be replaced by a cellulose-aceto-butyrates, which still contains free hydroxy groups.

Furthermore, there can be employed softeners of the type of phthalic acid ester.

Example 3

12 parts of benzylcellulose (54% of benzyl) are dissolved in a mixture of 66 parts of toluene and 22 parts of tetrahydrofurane. After adding 1.5 parts of oxalic acid-bis-phenylester being dissolved in some tetrahydrofurane, the lacquer is applied onto a support as described in the foregoing examples and then baked. It is not as easily soluble in pyridine as is a common benzylcellulose film.

Example 4

In case in Example 1 the sulfurous acid-bis-phenylester is replaced by an equal amount of

succinic acid-ortho-ethylester, there is obtained a coating which even at a temperature of 200° C is stable towards acetone and toluene.

Succinic acid-ortho-ethylester ($B_p 14 \text{ mm} = 113\text{--}116^\circ$) can be prepared from succino-bis-iminoether-chlorohydrate (see "Berichte der deutschen chemischen Gesellschaft," vol. 16, page 361) and alcohol in the cold.

Formic acid-o-ethylester can be used with a similar result.

Example 5

6 parts of acetylcellulose are dissolved in 54 parts of glykol-monomethyletheracetate. After the addition of 0.03 parts of p-toluene-sulfonic acid and 1 part of formaldehyde-di(β -chloroethyl)-acetal, being dissolved in the same solvent, the solution is treated as described in the foregoing examples. There is obtained an adhesive coating, which if contacted with acetone is only swollen.

SIEGFRIED PETERSEN.
KARL TAUBE.

ALIEN PROPERTY CUSTODIAN

HARDENING COLOPHONY

Reinard Ernst Vogel, Leutkirch (Allgau), Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 9, 1941

The present invention relates to a method of hardening colophony.

Various methods have become known already to improve after a longer heating upon an elevated temperature the hardness and water stability of colophony by the addition of soluble phenolic or other products of condensation which by themselves and without colophony may form hard and soluble products. Moreover, the melting point of colophony has been elevated with an alteration of other characteristic properties by the fact that colophony in the presence of solvents has been treated with volatile halides particularly with HCl, Al Cl₃, Ti Cl₄, BF₃ (see *Chemisches Zentralblatt* 1933, Volume II, Page 3628, French Patent 734,390 and 1935 Volume II, Page 135, German Patent 609,754).

Now a new way has been found to increase the hardness and the water stability of colophony by formaldehyde in the presence of strong organic acids. If colophony is heated for a longer period of time with formaldehyde for substances separating formaldehyde, for instance with a marketable formaldehyde solution, and with a polybasic organic acid, then after all the water has been removed and the melt has obtained a temperature up to 200°-210° C, a considerable elevation of the melting point and of the water stability is obtained. Nothing prevents esterification of the colophony at a temperature of 250° C. Formaldehyde loosely embedded in or added to colophony does not come into consideration in this case, because the so treated product has no longer the smell of formaldehyde or discharges such smell. All two—or three—basic organic acids also the inorganic hydrochloric acid in a percentage of 1-8% calculated to the resin may be employed. If no additional acid is used, then larger amounts of formaldehyde and considerable longer periods of reaction are required to obtain the same effect.

Example

	Parts
Colophony -----	30
Formaldehyde, 30% by weight-----	60
Oxalic acid -----	2.5

are boiled for 6 hours under reflux condensation and then the temperature is slowly raised during 3-4 hours to 210° C. The melting point of colophony raised from 58°-69° C. to 103°-109° C. The specific viscosity of a 40% solution spec/C in benzene amounted to 0.0306, whereas the same colophony with the same oxalic acid treated in the same manner but without the use of formaldehyde had a melting point of 63°-67° C. and a specific viscosity of spec./ C=0.0186, i. e. less than 39%.

According to the method disclosed in the German Patent 352,521 colophony is treated with furfural in the presence of acids. Furfural is a

heterocyclic aldehyde of the group of furfural and therefore behaves like an aldehyde and as an olefin oxide. In the heat furfural alone with acids forms resins (see American Patent 1,682,934) in contradistinction to formaldehyde. The German patent mentioned above, shows that in this case also no hardening of colophony occurs, but a resin formation of furfural is embedded, or, if in the most favorable case a hardening in the sense of a pure aldehyde would occur respectively the formation of furfural resin would inevitably result in parallel. Therefore, it cannot be concluded that formaldehyde may be employed instead of furfural. In all examples sulfur- or hydrochloric acid is used as catalyzer. The final product is a deep black resin (see page 1, line 17), whereas according to the method of the present invention no change of color of the colophony occurs.

In accordance with the method disclosed in the German Patent 203,847 operation is effected in such a manner that colophony is solved in alcohol and the formaldehyde is caused to act in the presence of a large amount of a strong acid in liquid form, for instance hydrochloric acid, formic acid or acetic acid. The hardening may occur at low temperature or at the boiling point of alcohol respectively (see page 1 lines 19-21). According to the method of the present invention, polybasic organic acids only are used by which the product is not dark colored as is the case in connection with hydrochloric acid, and which allow to effect the hardening in ordinary varnish boilers (formed of aluminium, nickel or stainless steels).

The method claimed in this case has, moreover, the great advantage that the process may be carried out without using solvents. From the begin it is not to be expected that without dissolving colophony in a solvent, i. e. in the melt, due to the presence of polybasic organic acids and anhydrous formaldehyde solutions only the hardness and viscosity of the resin is increased. Due to the mode of operation according to the present invention a separation of the finished resin from the solvent and the acid is rendered superfluous and the acid may either be used in this condition or be esterified at 250° C., for instance by means of glycerine.

The U. S. Patent 1,243,312 is concerned with the treatment of colophony with formaldehyde vapors without the use of catalyzers. The period of time for hardening is extremely long compared with the method carried out in the presence of organic polybasic acids besides the fact that special apparatus are required to produce the formaldehyde gas and to lead the latter into the liquid resin.

REINARD ERNST VOGEL.

ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCTS AND PROCESS OF PREPARING THEM

Herbert Bestian, Frankfurt am Main, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed July 22, 1941

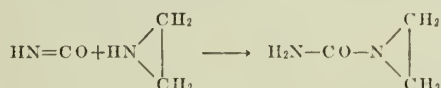
The present invention relates to a process of preparing condensation products and to the products thus obtained.

It is known to manufacture condensation products containing nitrogen by causing aliphatic isocyanic acid esters to react with alkylene imines, especially with ethylene imine.

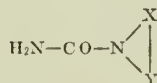
N'-alkyl-N.H-ethylene

ureas are thus formed.

Now I have found that water-soluble condensation products containing nitrogen are easily obtained in a very pure form by causing an alpha.beta-alkylene imine, especially ethylene imine to act upon isocyanic acid or an agent yielding isocyanic acid. The reaction occurs, for instance with respect to ethylene imine, according to the following formula:



The condensation products thus obtained are N.N-alkylene ureas of the general formula:



wherein



stand for an alkylene radical bound to the nitrogen atom in alpha.beta-position. Alpha.beta-alkylene imines are, besides ethylene imine, for instance, propylene imine, butylene imine, alpha.beta-decylene imine or other compounds. Products are thus obtained in which the cyclically

bound CH_2-CH_2 group may be substituted by aliphatic hydrocarbon radicals. The reaction which takes place with considerable evolution of heat is advantageously carried out in a solvent or a diluent. The said products are obtained in a well crystallized form and possess in the monomeric state an unlimited stability. From the N'-alkyl-N.N-alkylene ureas, obtained from the isocyanic acid esters and alkylene imines, they are distinguished by the fact that they possess an unsubstituted amino group, which renders further reactions possible, for instance the reaction with formaldehyde.

The compounds of the invention, especially N.N-ethylene urea, are suitable for various purposes of application. They may, for instance, be used as intermediate products or as valuable assistants in the textile, lacquer and rubber industry or the like.

The following example serves to illustrate the invention, but it is not intended to limit it thereto, the parts being by weight:

A solution of 43 parts of ethylene imine (boiling at $54^\circ\text{C}-56^\circ\text{C}$ under a pressure of 760 mm) in 50 parts of ether is run into a solution of 43 parts of isocyanic acid in 400 parts of ether, while stirring and well cooling. The temperature should not exceed 0°C . The N.N-ethylene urea formed during the reaction separates in a crystallized form and with a good yield. By recrystallization from acetone it is obtained in well-defined crystals and has in this form an unlimited stability. It is very readily soluble in water, soluble in alcohol and acetone and sparingly soluble in ether, benzene, benzene and carbon tetrachloride. It melts at 108°C .

HERBERT BESTIAN.

ALIEN PROPERTY CUSTODIAN

PREPARATION OF PHTHALOCYANINES

Hans Hoyer, Frankfurt A. M., Hans Colombara, and Berthold Bienert, Leverkusen-I. G. Werk, Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 24, 1941

The present invention relates to improvements in the preparation of phthalocyanines according to the so-called urea process.

It is known that phthalocyanines can be prepared by heating aromatic o-dicarboxylic acids or the corresponding anhydrides, ammonium salts, amides or imides with urea or heat-decomposition products thereof (other than ammonium) and a metal salt, for instance a copper salt, to a higher temperature. In many cases, this process is accompanied by an undesirable foaming of the melt. Thereby the disadvantage is involved that, owing to the high isolating capacity of foams, the reaction mixture can not be completely kept at the necessary reaction temperature. In consequence thereof, such processes are liable to yield a relatively low amount of the desired dyestuff.

It is the object of the present invention to do away with these advantages and to develop a modified urea process which allows one to prevent the formation of foams and to increase the yield of the desired phthalocyanine dyestuffs. Other objects of our invention will be apparent from the following description and claims.

It has been found that the disadvantages as explained above can be overcome by effecting the said process in the presence of such aromatic carboxylic acids or sulfonic acids or the amides thereof as are not capable of being converted into phthalocyanines. These auxiliary agents are effective only, as far as our hitherto experiments have shown, in the case of such phthalocyanine forming starting materials (i. e. aromatic dicarboxylic acids, amides, imides thereof etc.) as contain sulfonic acid groups or carboxylic acid groups in addition to those carboxylic acid groups which take part in the phthalocyanine forming reaction. Suitable auxiliary agents of the character described are, for instance, benzoic acid, benzene sulfonic acid, nuclear substitution products thereof and the amides of the said materials. Such auxiliary agents of the character described are preferred as are soluble in water either per se or in form of their alkali metal salts as such properties allow one to remove the said auxiliary agents from the melt after reaction by contacting the same with water or with a caustic soda lye. Depending on the nature of the starting materials and on the reaction conditions which are decisive for the more or less pronounced tendency of forming foams, the amount of the auxiliary agents may vary within wide limits. In general, an amount of about 20-30 per cent of the said auxiliary agents (calculated on the amount of the urea) is sufficient to exert the desired effect.

Generally, the efficacy of the said auxiliary agents is the better the higher the amount and the weight of the substituents which are present in the aromatic o-dicarboxylic acids. Benzamide has proved to be best suitable for the purpose in question.

Our invention is furthermore illustrated by the following examples, without, however, being restricted thereto:

Example 1

Into a melt of 70 g of urea there is added at a temperature of 140-145° C a mixture of

	Grams
Diphenyl-2,4,5-tricarboxylic acid-----	100
Benzoic acid-----	20
Copper chloride or an equimolecular amount of cobalt or nickel chloride-----	20

Thereupon, 0.6 g of ammonium molybdate are added and the melt is slowly heated to a temperature of 160-165°C, whereat a mixture of 100 g of urea and 20 g of benzoic acid is slowly added in such proportions that the melt never loses the capability of being agitated. The working up is effected by diluting the melt with water, rendering the same alkaline, removing the separated copper oxide and precipitating the phthalocyanine tetraphenyl tetracarboxylic acid by the addition of a mineral acid.

A similar result is achieved when using toluic or naphthoic acid instead of benzoic acid.

Example 2

Into a melt of 2.35 g of urea there is added while stirring at a temperature of 162-163° C a mixture of

	Grams
Urea -----	11.4
Potassium-4-sulfophthalate -----	11.4
Crystallized copper chloride-----	1.7
Ammonium molybdate-----	0.342
Benzoic acid -----	2.75

The melt is kept for about 4 hours at a temperature of 162-163° C, whereupon further 2.35 g of urea are added. After cooling down to about 100° C the melt is diluted with water, rendered slightly alkaline by means of caustic soda whereupon the so formed dyestuff is precipitated by the addition of sodium chloride. By redissolving the same from diluted hydrochloric acid there can be removed any traces of copper salts which might still be present therein.

The yield of dyestuff is 8 per cent higher than when working without benzoic acid.

Example 3

Into a melt of 7.5 g of urea there is added while stirring at a temperature of 162-163° C a mixture of

	Grams
Urea	15.0
Potassium 5 - benzoylamino-4-sulfophthalate	15.0
Crystallized copper chloride	1.53
Ammonium molybdate	0.45
Benzoic acid or m-chlorobenzoic acid, benzamide, N-monomethylbenzamide, p-toluene sulfonic acid or p-toluene sulfamide	6.75

The melt is kept for about 4 hours at a temperature of 162-163° C, whereat further 7.5 g of urea are added. A good yield of the corresponding copper phthalocyanine is obtained, whereat no foaming of the melt is observed.

Example 4

Into a melt of 5.2 g of urea there is added while stirring at a temperature of 162-163° C a mixture of

	Grams
Urea	21.9
Potassium-5-(2-chlorobenzoylamino)-4-sulfophthalate	21.9
Crystallized copper chloride	2.15
Benzoic acid	6.5
Ammonium molybdate	0.65

The melt is kept for about 4 hours at a temperature of 162-163° C, whereat further 5.2 g of urea are added. The melt does not foam, the corresponding copper phthalocyanine being formed in a yield of 67%, whereas the yield is about 37% in the case of working without benzoic acid.

Example 5

Into a melt of 3.9 g of urea there is added while stirring at a temperature of 180° C a mixture of

	Grams
Urea	7.8
Potassium-5-(2-chlorobenzoylamino)-4-sulfophthalate	7.8
Copper chloride or of an equimolecular amount of nickel chloride or cobalt chloride	0.765
Ammonium molybdate	0.235
p-Methoxybenzoic acid	2.34

The melt is kept for about 4 hours at a temperature of 180° C, whereat further 3.9 g of urea are added. The sodium 5,5',5''-(tetra-4-methoxybenzoylamino)-copper-phthalocyanine-4,4',4''-tetrasulfonate is obtained in a good yield.

HANS HOYER.
HANS COLOMBARA.
BERTHOLD BIENERT.

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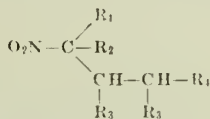
ALIPHATIC NITRO-COMPOUNDS

Otto Wulff, Königstein (Taunus), Heinrich Hopff
and Georg Wiest, Ludwigshafen am Rhein, Ger-
many; vested in the Alien Property Custodian

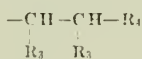
No Drawing. Application filed July 26, 1941

The present invention relates to aliphatic nitro-compounds.

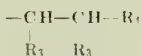
We have found that valuable aliphatic nitro-compounds may be obtained by condensing a nitrile or an ester, for instance the methyl-ester, ethyl-ester or propyl-ester of alpha-beta-unsaturated aliphatic carboxylic acids with primary aliphatic nitro-hydrocarbons. During the reaction of the nitriles, and this being surprising, just as many molecules of nitriles chiefly react with 1 mol of nitro-paraffine as active hydrogen atoms are contained in said nitro-paraffine. As starting material acrylic acid nitrile is particularly used; but moreover the corresponding alkyl derivatives are suitable, for instance crotonic acid nitrile and methacrylic acid nitrile as well as the esters of the corresponding acids. The products thus obtained have the following general formula:



wherein R_1 stands for a substituent of the group consisting of hydrogen, alkyl and



R_2 stands for a substituent of the group consisting of hydrogen and



one R_3 stands for hydrogen, the other R_3 for a substituent of the group consisting of hydrogen and methyl, R_4 stands for a substituent of the group consisting of $-\text{CN}$, $-\text{COO}-\text{H}$ and $-\text{COOR}_5$, R_5 being alkyl.

As nitro-hydrocarbons there may, for instance, be used nitro-methane, nitro-ethane, 1-nitro-propane, 1-nitro-butane or 1-nitro-pentane.

Alkaline substances, such as potassium carbonate, sodium carbonate, caustic soda solution, lime, sodium alcoholate, pyridine and the like have been found suitable as condensing agents. The addition of a solvent or diluent may be advantageous for moderating the reaction and bringing all the components into one phase. It may also be suitable first to introduce the nitrile or the ester and then to cause the nitro-hydrocarbon gradually to run in.

The nitro-polycarboxylic acid nitriles and nitropolycarboxylic acid esters obtained may be used as softening agents or as solvents. If neces-

sary, the nitro-nitriles and nitro-esters are saponified to obtain the corresponding nitro-polycarboxylic acids. The saponification, and this being surprising, readily occurs and the nitro-group is not impaired thereby. Furthermore amino-polynitriles or amino-polycarboxylic acids and the corresponding lactams as well as polyamines are obtained by a reduction or a catalytic hydrogenation. By mild conditions of hydrogenation the corresponding hydroxyl-amino compounds are likewise obtainable. All these substances are of great industrial importance when they are used as such or as intermediate products for softening agents, resins, adjuvants in the textile industry and in the pharmaceutical industry.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

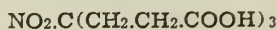
(1.) An aqueous solution of 30 grams of potassium carbonate is introduced at a temperature of 15°C – 20°C , while stirring, into 1200 grams of acrylic acid nitrile, 1100 grams of alcohol and 450 grams of nitro-methane, whereby reaction sets in with self-heating up to 30°C . Further 450 grams of nitro-methane and an aqueous solution of 30 grams of potassium carbonate are then introduced in the course of about 5 hours at 30°C , while stirring. The mixture is then kept for several hours at 40°C . After 1 to 2 days the large crystals which have separated are filtered with suction, washed and dried. A further portion of crystals is obtained by the addition of water to the filtrate. The yield amounts to 860 grams of nitromethyl-tri-beta-propionic acid nitrile $\text{NO}_2\text{C}(\text{CH}_2\text{CH}_2\text{CN})_3$, i. e. 52 per cent of the theoretical yield. White, great prisms are obtained which are sparingly soluble in water and alcohol and melt at 110°C to 112°C .

The corresponding mono-substitution products and di-substitution products (γ -nitro-butyric acid nitrile boiling at 118°C – 121°C under a pressure of 3 mm of mercury and nitromethyl-di-beta-propionic acid nitrile $\text{NO}_2\text{CH}(\text{CH}_2\text{CH}_2\text{CN})_2$, melting at 60°C – 63°C) are likewise obtained in very small proportions, but only when the nitro-methane is used in a very large excess.

Saponification of the nitro-methyl-tri-beta-propionic acid nitrile

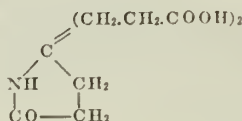
165 grams of nitro-methyl-tri-beta-propionic acid nitrile are boiled for 4 hours in a reflux condenser together with a mixture of 1 kilogram of concentrated hydrochloric acid and 600 cc of

water. When cold the corresponding nitro-methyl-tri-beta-propionic acid



crystallizes. The yield amounts to 185 grams, i. e. 90 per cent of the theoretical yield. The product melts at 183° C to 186° C.

By a catalytic hydrogenation of said nitro-tri-carboxylic acid the corresponding amino-tri-carboxylic acid or the lactam



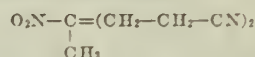
immediately formed therefrom by the separation of water and melting at 159° C-161° C are obtained in a good yield.

Further products may be obtained by a reduction or a catalytic hydrogenation of the nitro-methyl-tri-beta-propionic acid nitrile, for instance aminomethyl-tri-beta-propionic acid nitrile and poly-amines.

(2.) 80 grams of acrylic acid nitrile, 80 grams of alcohol and 38 grams of nitro-ethane are mixed, while stirring. By the addition of a solution of 2 grams of potassium carbonate in 15 cc of water the reaction is started at 12° C-15° C.

With self-heating to 40° C-45° C the reaction is chiefly complete after about 1 hour; it is terminated by further heating it for 5 hours to 40° C.

By the addition of water the reaction product is separated in the form of an oil which is washed and dried. Acrylic acid nitrile present in excess is removed by distillation under reduced pressure. The residue from distillation is a thick brownish oil and constitutes the 1-nitro-ethyl-1-di-beta-propionic acid nitrile



It can be distilled only with decomposition. The yield amounts to 60 grams, i. e. 67 per cent of the theoretical yield. If nitro-ethane is used in a large excess there is likewise obtained the 7-nitro-valeric acid nitrile in the form of an oil boiling at 106° C under a pressure of 2 mm of mercury.

By boiling the 1-nitro-ethyl-1-di-beta-propionic acid nitrile with a strong acid the corresponding 1-nitro-ethyl-1-di-beta-propionic acid is obtained.

OTTO WULFF.
HEINRICH HOPFF.
GEORG WIEST.

ALIEN PROPERTY CUSTODIAN

STABLE DISPERSIONS

Werner Starck, Hofheim (Taunus), Germany;
vested in the Alien Property Custodian

No Drawing. Application filed July 26, 1941

The present invention relates to stable dispersions.

It is known that for preparing dispersions of highly molecular substances the polymerization of the monomers, for instance of the vinyl compounds, may be carried out in aqueous solutions of surface-active soap-like emulsifiers. As suitable for this purpose there are mentioned, for instance, salts of fatty acid such as sodium oleate, or alpha-hydroxy-octodecane sulfonate of sodium; furthermore: the water-soluble products of strong emulsifying action which have been prepared by addition of ethylene oxide to fatty alcohols or alkyl-substituted phenols. The use of such emulsifiers in the polymerization, however, involves the drawback that as a rule it is not possible to obtain aqueous dispersions containing, for instance, more than 30% of polyvinylacetate.

On the other hand it has already been proposed in U. S.-patent application Serial No. 276,224, filed May 27, 1939, by J. A. A. Heuer as administratrix of Werner Heuer, deceased, for "Polymerization products and aqueous emulsions thereof" to introduce into the polymolecule small amounts of vinylsulfonic acid and the salts thereof. By introduction of the $-\text{SO}_3\text{H}$ -group which has an emulsifying action it is possible to carry out the polymerization in an aqueous medium without application of additional emulsifying agents and thus to obtain relatively stable dispersions of the polymerizates. The concentration, however, of the dispersions thus obtained is limited to at most about 50%. The diameters of the resultant particles of the dispersion are of the order of magnitude of about $0.5-1\mu$. The films obtained by drying such emulsions are turbid and sensitive to water.

The object of the present invention are dispersions of the interpolymerization products described in the above mentioned U. S.-patent application, which dispersions are very stable and of particularly high concentration. Besides the interpolymerization products mentioned in the said U. S.-patent application which are prepared from vinylsulfonic acid or the water-soluble salts thereof and polymerizable compounds containing the group



These dispersions contain emulsifying agents. Such dispersions are obtained, above all, by carrying out the polymerization of the monomers, for instance the vinyl compounds, in an aqueous medium with addition of vinylsulfonic acid or the

salts thereof and in the presence of emulsifiers, for instance of soap-like nature. In this way dispersions of a paste-like consistency and of hitherto unattainable concentrations of 60% and more may be obtained. These latices contain the polymers in a state of extraordinarily high dispersion, a fact which is revealed even by a short inspection, they diffract the light rays to a high degree, and exhibit a play of colors. The size of the particles of the dispersed phase amounts to about 0.1 to about 0.2μ . By drying up such dispersions, entirely clear transparent films are obtained which are insensitive to water.

It is surprising that by simultaneous introduction of the hydrophilic vinylsulfonic acid group during the polymerization with emulsifiers, stable dispersions containing a high percentage of the polymerization product are obtained which may be dried with formation of such water-proof films that new fields are opened for the application of these products.

The polymerization may be performed in the manner usual for polymerizing, for instance, vinyl compounds, for example, by heating in the presence of a catalyst such as hydrogen peroxide, potassium persulfate, benzoyl peroxide or oleyl peroxide.

As water-soluble salts of vinylsulfonic acid of the formula $\text{H}_2\text{C}=\text{CH}.\text{SO}_3\text{H}$ there may, for instance, be mentioned: the sodium salt, the potassium salt and the ammonium salt; furthermore, the salts of amines, such as methylamine, dimethylamine, ethylamine, diethylamine or

Other polymerizable compounds which may be used in the process of this invention are those containing the group



especially vinyl compounds. Suitable compounds are, for instance, vinyl acetate, vinyl formate, vinyl propionate, vinyl butyrate, vinylbenzoate, vinyl chloride, acrylic acid methyl ester, acrylic acid ethyl ester, acrylic acid propyl ester, methacrylic acid methyl ester, methacrylic acid ethyl ester, methacrylic acid propyl ester, vinyl ketones such as vinylmethyl ketone, styrene, and vinyl ethers such as vinylbutyl ether. Mixtures of two or more of these monomers may also be used. Small quantities of the vinylsulfonic acid are preferably applied, for instance, 0.05 to 5%, calculated upon the weight of the polymerizate.

As emulsifiers there may be used quite generally anion-active, neutral and cation-active emulsifiers. There may be mentioned, for instance,

soaps, that is to say, alkali metal salts of higher molecular fatty acids, naphthenic acids or resinic acids; aromatic sulfonic acids especially sulfonic acids of alkyl-substituted aromatic hydrocarbons, for instance, dibutyl-naphthalene sulfonic acid; sulfonation products of fatty acids or derivatives thereof, for instance, castor oil; sulfates of aliphatic alcohols, for instance, dodecylalcoholsulfate; paraffin-C-sulfonic acids, for instance, the compounds obtainable by saponification of products obtainable by the action of sulfur dioxide and chlorine on aliphatic hydrocarbons; condensation products of fatty acids with amino- or hydroxysulfonic acids or-carboxylic acids, for instance, the condensation product of oleic acid chloride and taurine; condensation products of ethylene oxide or alkylene oxides with higher molecular organic compounds containing hydroxy-, amino-, carboxyl-, mercapto- groups, especially condensation products of ethylene oxide with aliphatic alcohols or with phenols being substituted in the nucleus by higher molecular radicals or the sulfonation products of these compounds; salts of high-molecular amines, such as the hydrochloride of octodecylamine; finally quaternary ammonium compounds, betaines or the like.

As emulsifiers there are suitable, among others, the addition product of 30 mols of ethylene oxide to oleyl alcohol and the sodium alpha-hydroxy-octodecane sulfonate.

Moreover, it is possible to add softeners such as phthalic acid ester or phosphoric acid ester or other auxiliary agents before, during or after the polymerization. Preferably the polymerization is carried out by introducing, while stirring and heating, into the aqueous liquid containing the emulsifier, a salt or vinyl-sulfonic acid and the catalyst, for instance, potassium persulfate, the monomer *pari passu* with the progressive exothermic polymerization. It is also possible to emulsify the aqueous and the organic phases in the cold by quickly stirring and, thereupon, to polymerize this emulsion by cautiously heating. If desired, the polymerization may also be carried out in the presence of small quantities of solvents for the dispersed products, the quantities amounting to about 3 to about 5% calculated upon the total weight of the dispersion.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight:

(1) 2 parts of potassium persulfate and 2 parts of sodium vinylsulfonate are dissolved in 200 parts of a 3% aqueous solution of the condensation product of 30 mols of ethylene oxide and oleyl alcohol. The solution is heated to 75° C in a

vessel provided with a reflux apparatus and a stirrer. 300 parts of vinylacetate are then caused to run in, in the course of 3 hours, the reflux being only feeble. Shortly after the beginning of the introduction, polymerization sets in which becomes apparent by the fact that the contents of the vessel become white. When the introduction is finished, the whole is heated for ½ hour. The dispersion obtained has the consistency of a thick cream, shows a red-green fluorescence and dries with formation of a water-proof clear film.

(2) As aqueous liquid there are used 175 parts of a 3% solution of sodium alpha-hydroxy-octodecane sulfonate to which 1 part of ammonium persulfate and 3 parts of sodium vinylsulfonate are added. Within 2 hours, there is introduced into this solution, as described in example 1, a mixture of 240 parts of vinylacetate, 45 parts of vinylbenzoate, 26 parts of tricresylphosphate, 13 parts of phthalic acid dibutylester and 10 parts of methanol. The dispersion is obtained in the form of a thick paste which may well be spread and which, after freezing to -20° C and defreezing, has again its original consistence. By drying the dispersion, films are obtained, which are clear as water, very supple and are not rendered turbid by water-drops.

(3) 6 parts of the condensation product of 6 parts of ethylene oxide with butylphenol, 2 parts of vinylsulfonic acid and 1 part of potassium persulfate are dissolved in 200 parts of water. A mixture of 210 parts of vinylacetate and 70 parts of acrylic acid butyl ester is emulsified in this solution, while quickly stirring. The emulsion obtained is introduced in the course of 2 hours and while stirring, into a vessel heated to 70° C and provided with a stirrer. A creamy polymerization-dispersion is obtained which is highly dispersible and dries with formation of a well-pliable film clear as water.

(4) 3 parts of sodium persulfate and 4 parts of ammonium vinyl-sulfonate are dissolved in 300 parts of a 4% aqueous solution of the condensation product from 30 mols of ethylene oxide and octodecylalcohol. While quickly stirring, 700 parts of acrylic acid methylester are emulsified in this solution. There is obtained a stable emulsion of the monomeric ester which is introduced in the course of 3 hours, while slowly stirring, at a temperature of the bath of 70° C into a vessel provided with a reflux apparatus and a heating device. When the reaction is finished, heating is continued for ½ hour. A stable, creamy dispersion is obtained which dries with formation of entirely clear films.

WERNER STARCK.

ALIEN PROPERTY CUSTODIAN

DRY POLYMERIZATION PRODUCTS

Werner Starck, Hofheim (Taunus), and Wilhelm Spiecker, Frankfurt am Main-Hoechst, Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 26, 1941

The present invention relates to substantially dry compositions of matter containing synthetic polymerization products; more specifically it relates to compositions which show the remarkable property of being easily and completely distributable to form stable aqueous dispersions when agitated with water or aqueous media. The preferred embodiment of the invention are dry preparations of polyvinyl compounds, more particularly polymerization products of compounds having the group



and interpolymerization products of said compounds.

Synthetic polymerization products, especially polyvinyl compounds, are widely applied in the form of aqueous dispersions; this mode of application has the advantage that the polymerization products may be used in the liquid phase and that, thereby, the numerous drawbacks involved in the use of organic solvents are avoided.

It has, however, in practically all cases proved to be very difficult for the consumers of hitherto known polymerization products to prepare aqueous dispersions thereof, since the dispersing of said products requires knowledge and apparatus commonly not available to the majority of the industries consuming and applying plastics.

The manufacturers of synthetic polymerization products, therefore, proceeded to prepare and to market aqueous dispersions of said products even though the transportation of the large amounts of water proved to be very uneconomical, quite apart from the fact that sometimes the aqueous dispersions coagulate during transportation or storing, thus causing further inconvenience.

Now, it has been found that it is possible to obtain, by drying aqueous dispersions of polymerization products, powders of such a form that they may again be emulsified in water with formation of dispersions having the same properties as the dispersions originally used. To this end, dispersions of such polymerization products are used as are prepared by means of water-soluble high-molecular protective colloids. As products suitable for the purpose of the present invention there are mentioned: polyvinyl alcohol and the water-soluble derivatives thereof, such as, products partially esterified with formic acid, acetic acid, propionic acid or butyric acid, products partially acetalized with formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde or cyclohexanone, in which cases, however, only

such a number of ester-, aldehyde-, or keto-groups may be present that the products are still water-soluble; furthermore, polyethylene oxide, salts of polyacrylic acid or of polymethacrylic acid, for instance, the ammonium, potassium or sodium salts of these acids; or the salts of interpolymerization products from maleic acid or crotonic acid and vinyl compounds as well as the water-soluble amides of polyacrylic and polymethacrylic acid. Such dispersions are described in USA patent No. 2227163.

As polymerization products which may be worked up to form dry preparations there may be mentioned, for instance: polymerization and interpolymerization products of vinylacetate, vinylformate, vinylpropionate, vinylbutyrate, vinylbenzoate; furthermore, vinylchloride; acrylic acid- and methacrylic acid methylester, acrylic acid- and methacrylic acid ethylester, acrylic- and methacrylic acid propylester; vinylmethylketone, styrene, vinyl ether as well as vinylbutyl ether.

It is advisable to effect the drying under conditions as mild as possible so that the emulsifying property of the water-soluble emulsifier is not affected thereby. Therefore, the drying is performed advantageously at a temperature as low as possible, if necessary, under reduced pressure. In order to prevent the moist or dry particles of the polymerization products to adhere to each other, the temperature is not allowed to rise up to the point at which the particles begin to sinter or even to melt. Furthermore, it is advisable to adjust the dispersions to a neutral pH-value prior to the drying. As drying processes there may be applied, besides the known processes carried out under reduced pressure, spray-dryings, for instance, according to the "Krause" or "Nubilosia" systems. Such drying processes are, for instance, described in "Chemische Apparatur," vol. 28, No. 4, pages 49-52. Furthermore, it is also possible to freeze the aqueous dispersions and, thereupon, to dry them with application of reduced pressure and of drying agents, for instance, concentrated sulfuric acid or calcium chloride.

It could not be foreseen that it would be possible to dry aqueous dispersions of hydrophobic or thermoplastic masses with formation of powders yielding again, when agitated with water, stable finely disperse latices of original quality especially in view of the fact that the emulsifiers used are present only in small quantities of, for instance, 2-3% calculated upon the polymer. The effect is all the more surprising because coagulates which are often formed in the prep-

aration of such dispersions cannot be converted by means of water into the desired highly disperse state.

The use of polymerization products in the form of their aqueous dispersions has recently found a wide field of application. For instance, coated or finished fabrics, synthetic leather-like products prepared from leather- or textile fibers as well as coating agents are prepared to a large extent by means of such synthetic latices. In all these cases it is of great technical advantage that one may start from solid, particularly from pulverized, products since, as above stated, it is thereby possible to reduce the costs of freight and packing when the goods are transported; furthermore, losses due to the formation of skins and crusts are avoided and the consumer is in the position to adjust the synthetic latex to any desired concentration directly before use. The latices in question are prepared by introducing the dry powders into the desired quantity of water while agitating, for instance, while well stirring. The usual auxiliary agents such as softeners, pigments or filling agents may then be added as desired, while stirring.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

(1) A highly viscous 50% dispersion of polyvinylacetate prepared according to one of the usual methods by polymerization of vinylacetate with the same quantity of a 5% aqueous solution of polyvinyl alcohol and consisting of particles of $0.5-2\mu$, is poured on drying sheets to form layers of 2-3 cm thickness which are frozen at -10°C . In this form the sheets are placed in a drying-oven in which a pressure of 0.1 mm is maintained by means of an efficient pump. A vessel containing concentrated sulfuric acid serves as receiver.

The aggregate is kept at room temperature for 24 hours. In this way a product is obtained which is practically free from water and may easily be pulverized by means of a comminuting apparatus. When the powder thus obtained is introduced into water, while stirring, a highly-viscous dispersion like that originally used is obtained.

(2) The dispersion used in example 1 is diluted with water to a dry contents of 40% and adjusted to a pH-value of 7. In a "Nubilos" drying apparatus the dispersion is atomized by means of air of $+12^{\circ}\text{C}$, care being taken that the inferior part of the tunnel drier is kept at low temperature by external cooling.

A powder fine as flour is obtained which, when stirred with water, again yields a stable latex. Into the latter the desired quantity of softener may be introduced, by stirring quickly. The emulsion obtained is suitable for preparing coated or finished fabrics or the like.

Instead of the "Nubilos" apparatus there may be used with the same success a "Krause" drier; in the latter case, the temperature of the air advantageously amounts to $40^{\circ}\text{C}-50^{\circ}\text{C}$.

(3) Into a 45% dispersion prepared by means of an interpolymerization product from 70 parts by weight of vinylacetate and 30 parts by weight of vinylchloride and an aqueous 3% solution of sodium polyacrylate, there are introduced 2% of ammonium carbonate, calculated upon the dry substance. The dispersion is then atomized by means of a "Nubilos" or a "Krause" drier as described in example 2. By means of water the fine powder obtained may be re-transformed into a finely dispersed latex which is ready for use.

WERNER STARCK.
WILHELM SPIECKER.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF CARBOXYLIC ACIDS OF THE PYRIDINE SERIES

Heinrich Hopff and Wilhelm Rapp, Ludwigs-hafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 26, 1941

The present invention relates to a new process for the production of carboxylic acids of the pyridine series.

Carboxylic acid esters of the pyridine series, such as collidine dicarboxylic acid esters, are known to be difficultly attacked by aqueous solutions of alkali metal hydroxides, even if kept boiling for some time. Their saponification with alcoholic caustic alkali solutions proceeds smoothly but in this case the drawback exists that the alkali metal salts, in order to recover the free acids, must be converted into the lead or silver salts from which the acids are liberated by means of hydrogen sulphide. Such a multi-stage process, however, is uneconomic and, moreover, does not give satisfactory yields.

We have now found that carboxylic acid esters of the pyridine series can be converted into the free carboxylic acids in a simple manner and with good yields by heating the esters in the presence of water under pressure at a temperature of at least about 150° C. This course of the reaction is surprising since the esters are difficultly attacked even by aqueous solutions of alkali hydroxides, as stated above.

According to the present invention it is possible to obtain pyridine mono-, -di- and -polycarboxylic acids or their homologues, as for example lutidine-mono- or -dicarboxylic acid or collidine-mono- or -dicarboxylic acid, from their esters. Since in the synthesis of compounds of the pyridine series such esters are directly obtained (for example collidine dicarboxylic acid esters by condensing aldehyde-ammonia with acetic acid ester and oxidizing the dihydrocollidine dicarboxylic acid ester first obtained) the process according to the present invention provides a simple way for preparing the free carboxylic acids of the pyridine series.

The saponification is carried out, for example, at a temperature of between 150 and 200° C. The amount of water employed is advantageously from 4 to 6 times that of the ester. Usually the

reaction mixture is simply heated in a closed vessel. The pressure may, however, be increased by pressing inert gases into the reaction space. After cooling, the greater part of the acids formed frequently crystallizes out and may be obtained by filtration, by centrifuging etc. An additional amount of carboxylic acid can be obtained by concentrating the mother liquor, if desired in vacuo.

The following examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to the said examples. The parts are by weight.

Example 1

400 parts of collidine dicarboxylic acid diethyl ester and 2500 parts of water are heated in an iron pressure vessel for 24 hours at from 160° to 180° C. After cooling, the main part of the collidine dicarboxylic acid formed has crystallized out and is filtered off. By evaporating the mother liquor down to half its volume further acid is obtained. By recrystallizing the crude product from a little water while adding animal charcoal, 120 to 140 parts of pure collidine dicarboxylic acid are obtained crystallizing in the form of fine felted needles. As bye-products collidine monocarboxylic acid and collidine are recovered.

Example 2

30 parts of nicotinic acid ethyl ester and 180 parts of water are heated at a temperature of from 150° to 160° C for 20 hours. On cooling the reaction mixture, part of the nicotinic acid crystallizes out which is filtered off. A further amount of acid may be caused to crystallize by concentrating the mother liquor to half its volume. About 13 to 14 parts of nicotinic acid are obtained. By recrystallizing it from water it is obtained in a pure state.

HEINRICH HOPFF.
WILHELM RAPP.

ALIEN PROPERTY CUSTODIAN

POLYVINYL CHLORIDE COMPOSITIONS

Friedrich Manchen, Mannheim, and Willi Schmidt, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 29, 1941

This invention relates to new polyvinyl chloride compositions containing polyvinyl chloride, which expression is intended to cover also interpolymerisation products of polyvinyl chloride with other vinyl compounds, and, as a plasticizer therefor, fatty acid esters of aliphatic polyhydric alcohols.

We have found that certain esters of fatty acid mixtures and polyhydric alcohols which are obtained by esterifying triethylene glycol or other aliphatic polyhydric alcohols or mixtures of such alcohols, the average molecular weight of which corresponds substantially to that of triethylene glycol, with mixtures of at least two fatty acids containing at least 4 and at most 12 carbon atoms, in other words aliphatic monocarboxylic acids having an average acid-number between 350 and 430, are most suitable as plasticizers in the preparation of compositions from polyvinyl chloride and its interpolymerisation products with other vinyl compounds, in particular with unsaturated esters, e. g. vinyl esters of organic acids and acrylic and methacrylic acid esters.

In the preparation of these esters there may be used triethylene glycol itself, furthermore polyhydric aliphatic alcohols having a molecular weight in the neighbourhood of that of triethylene glycol, say between 140 and 180. Such glycols are, for example, hexanetriol, dipropyleneglycol or mixtures of various ethylene glycols which contain in addition to triethylene glycol either di- or tetraethylene glycol or both of these glycols and which have an average molecular weight corresponding substantially to that of triethylene glycol itself.

The fatty acid mixtures used in the preparation of the plasticizers according to our invention contain at least two, preferably at least 3 carboxylic acids of different length of chain. Mixtures of heptane, octane and nonane carboxylic acid, for example, are particularly useful; mixtures of other fatty acids having from 4 to 12 or from 5 to 11 or 12 carbon atoms may also be employed. Such mixtures may be obtained by admixing individual carboxylic acids of natural or synthetic origin with one another or by the oxidation of paraffin wax or other aliphatic hydrocarbons or hydrocarbon mixtures whereby mixtures of different carboxylic acids are formed. The carbon chain of these acids may be straight or branched.

From these polyhydric alcohols and these fatty acids neutral esters, i. e. those containing two carboxylic acid radicles for one radicle of the polyhydric alcohol, may be prepared in any usual

manner. A mixture of equivalent amounts of the polyhydric alcohol with the fatty acid mixture may be heated, if desired in the presence of catalysts, e. g. concentrated sulfuric acid, phosphoric acid and the like. The water formed should be removed continuously by azeotropic distillation.

When admixing the esters with polyvinyl chloride or polyvinyl chloride-containing compositions such as interpolymerisation products of vinyl chloride with vinyl esters of organic acids, e. g. vinyl acetate, vinyl ethers, acrylic or methacrylic acid esters, e. g. methyl, ethyl, propyl or butyl acrylate, acrylic nitrile, styrene and the like, plastic masses are obtained which are excellently stable to cold and heat. The esters are compatible with polyvinyl chloride and polyvinyl chloride compositions in exceptionally high amounts. Due to their high gelatinizing power, they may easily be compounded with polyvinyl chloride. In these plastic compositions part of the plasticizer according to our invention may be replaced by the common softeners heretofore known, such as glycerol triacetate, dimethyl phthalate and other phthalic acid esters, or triaryl phosphates.

The compositions may be prepared in any known manner with or without the usual volatile solvents or diluents, which are satisfactorily compatible with the plasticizers. By kneading or rolling mixtures of vinyl chloride with the ester at elevated temperature homogeneous plastic compositions are easily obtained.

The plasticizer according to our invention may, if desired, be added to vinyl chloride or mixtures thereof with other polymerizable vinyl compounds before polymerization.

The compositions according to our invention are useful in the preparation of various articles obtainable by extruding, casting, molding, injection-molding and the like. They are suitable in the production of sticking agents or lacquers for coating metal, leather, paper, fibrous material and wood, in the production of rods, tubes, films, foils, safety glass, artificial leather and the like. In the preparation of these articles, the common filler bodies, pigments, coloring agents or stabilizing agents may be added.

The following examples will further illustrate how this invention may be carried out in practice. The invention, however, is not restricted to these examples. The parts are by weight.

Example 1

30 parts of the ester obtained by esterifying

375 parts of triethylene glycol with 705 parts of a fatty acid mixture, having an acid number of 398 and containing acids with from 5 to 11 carbon atoms, are admixed with 70 parts of polyvinyl chloride. The mixture is rolled in a rolling-mill at 155-165° C. A rubber-like homogeneous composition is thus obtained having excellent durability and high fastness to cold. It may be used in the preparation of artificial leather.

Example 2

137 parts of a mixture containing 32 parts of diethylene glycol and 105 parts of triethylene glycol are esterified with 300 parts of a fatty acid mixture, having an acid number of 376 and containing acids having from 5 to 12 carbon atoms. 60 parts of this ester are intimately mixed with 100 parts of the interpolymerisation product from 84 parts of vinyl chloride and 16 parts of acrylic acid methyl ester and homogenized in a rolling-mill at 140-150° C. A plastic and elastic composition is obtained which is stable to cold and will withstand ordinary usage satisfactorily for a long time. It may be used for insulating cables.

Example 3

A mixture of 40 parts of polyvinyl chloride and 20 parts of the interpolymerisation product described in Example 2 are admixed with an ester obtained by esterifying 89 parts of a mixture of ethylene glycols, having an average molecular weight of 177, with 141 parts of the fatty acid mixture referred to in Example 1. To this mixture there are added from 20 to 40 parts of a

filler, e. g. calcium carbonate, kaolin, slate-powder, carbon black or titanium dioxide. The whole is homogenized in a rolling-mill at 140-160° C. The plastic composition has excellent durability and stability to cold. It may be used for coating the surface of tanks, cans and other receptacles or for floor-covering.

Example 4

10 50 parts of polyvinyl chloride and 50 parts of the ester described in Example 1 are intimately mixed by stirring at room temperature. The viscous dispersion of polyvinyl chloride in the plasticizer thus obtained may be homogenized by heating to 155-165° C. A soft elastic composition is obtained which is excellently stable to cold and storage. It may be used for coating fabrics or metal surfaces or for molding purposes.

Example 5

20 25 parts of a plasticizer obtained by the esterification of 120 parts of triethylene glycol with 240 parts of a fatty acid mixture, having an acid number of 387 and containing acids with from 7 to 9 carbon atoms, are admixed with 75 parts of the interpolymerisation product from 80 parts of vinyl chloride and 20 parts of acrylic acid methyl ester and homogenized in a rolling-mill. The resulting plastic composition is elastic and stable to cold and storage. It may be used for coating materials, in particular for the preparation of water-proof fabrics or artificial leather.

FRIEDRICH MANCHEN
WILLI SCHMIDT.

ALIEN PROPERTY CUSTODIAN

COMPOSITION OF MATTER COMPRISING CELLULOSE ESTERS

Georg Spielberger, Leverkusen-I. G. Werk, and
Reinhardt Hebermehl, Köln-Deutz, Germany;
vested in the Alien Property Custodian

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The present invention relates to a new composition of matter comprising cellulose esters of lower aliphatic carboxylic acids.

It is known that film-forming materials such as cellulose esters, in order to be suitable for the preparation of lacquers, coating materials and the like, require the incorporation therewith of resins. The presence within such film-forming materials of resins effects an increase of the adhesive properties of the films prepared therefrom if applied to a support and of the brightness of the coatings. Resins, in order to be suitable for the purpose in question, must be compatible with the film-forming materials within wide limits and, moreover, must be stable towards light to a far reaching degree. As far as cellulose esters of lower aliphatic acids are concerned, there is a lack of resins which combine these properties without being accompanied by other disadvantages. Thus, products of the condensation of formaldehyde and aromatic sulfonamides, such as benzene or toluene-sulfonamide, which have been mostly employed for the purpose in question, are relatively sensitive towards water, thus impairing the properties of the cellulose ester coatings. It is owing to this lack of suitable compatible resins that cellulose acetate and other cellulose esters with lower aliphatic acids, though being distinguished by an excellent fastness to light, have not been employed to a great extent within the coating and lacquer industry.

It is the object of our present invention to develop new resins which are compatible with such cellulose esters within wide limits and combine this compatibility with a good fastness towards water and light and with all such other properties as are required for the purpose in question. Other objects of our invention will be apparent from the following description and claims. Our invention in its broadest aspect relates to a composition of matter comprising cellulose esters of lower aliphatic carboxylic acids and formaldehyde-monoarylurea-condensation products. Condensation products of the character described are insoluble in aliphatic and aromatic hydrocarbons and soluble in those solvents such as ketones, esters, glycolmonoalkyl-ethers or chlorine containing hydrocarbons and alcohols which are usually employed for dissolving of cellulose esters. The softening point of such products is preferably between about 50 and about 100° C. They are capable of being homogeneously incorporated within cellulose esters up to a proportion of about 150%. Moreover, they are not materially colored and combine this property with a good fastness to light and to water. This is true of the pure monoarylurea-formaldehyde-condensation products as well as of those mixed condensation products which have been prepared from formalde-

hyde on the one hand and a mixture of a monoarylurea and another formaldehyde-reactive compound, provided that the monoarylurea is present therein in a preponderant amount. Suitable formaldehyde-reactive compounds for the purpose in question are, for instance, aryl-sulfonamides such as benzene- or toluyl-sulfonamide. As monoarylurea, there is preferred the non-substituted phenylurea, although substitution products thereof, such as a uniform toluyl-urea or xylyl-urea or mixtures of the isomeres thereof, are not excluded. Furthermore, there can be employed halogen-substituted phenyl ureas.

As cellulose ester, there is preferably employed the so-called secondary cellulose acetate, i. e. the product obtained from the primary cellulose triacetate by a partial saponification, furthermore, the primary cellulose triacetate itself, cellulose propionate and cellulose butyrate and mixed esters of the said acids.

As a matter of fact, the composition of matter described may also contain softeners such as triarylphosphates, trichloroethylphosphate, dialkylphthalates and, furthermore, pigments, dye-stuffs, filling materials and the like.

The condensation products which are made use of in the preparation of our new compositions of matter can be prepared in the usual manner by causing formaldehyde to react upon a monoarylurea, the reaction being preferably started in an alkaline medium, for instance at a pH-value between about 8 and about 9, and finished at a pH-value between about 4 and about 8. The reaction temperature is preferably kept between about 60° and about 100° C, the condensation products being isolated from the aqueous medium by evaporation. Depending on the choice of the starting materials and on the degree of condensation, the softening point is between about 40 and about 110° C, the compatibility of the condensation products with cellulose esters being decreased with a rising of the softening point.

Our invention is furthermore illustrated by the following examples without, however, being restricted thereto, the parts being by weight:

Example 1

135 parts of phenylurea are heated for one hour at 90-100° C with 350 parts of a 33% solution of formaldehyde which has been rendered alkaline by means of sodium hydroxide. The resin thus formed is isolated by evaporating the water in vacuo. The heating in vacuo is continued until the resin has assumed a temperature of 120° C. The colorless resin having a softening point of 83-84° C according to the method of Krämer-Sarnow-Nagel is dissolved in cyclohexanone so as to form a 20% solution.

parts of this solution if added to an acetylcellulose lacquer of the following composition:

	Parts
Acetylcellulose -----	12
Methylacetate -----	9
Ethylacetate -----	4
Methanol -----	5
Ethylalcohol -----	15
Toluene -----	15
1-methoxy-2-acetoxy-ethane -----	40

yield a clear solution from which there is obtained after evaporation of the solvents a homogeneous clear film of an excellent adhesive capacity.

Example 2

405 parts of phenylurea are heated for half an hour at 95° C with 1050 parts of a 30% formaldehyde solution containing 1.5 parts of anhydrous sodium carbonate. After the addition of 2.25 parts of tartaric acid the solution is cooled to 50° C and filtered. By evaporating in vacuo at a temperature of 90° C, 500 parts of a colorless blistery resin are obtained. The following lacquer is prepared therefrom:

	Parts
Resin -----	8
Celluloseacetobutyrate -----	8
Tributylphosphate -----	2
Benzylbutylphthalate -----	2
Diglycolic acid butylene glycolic ester -----	0.5
Ferric hydroxide -----	8
Acetone -----	32.5
Toluene -----	13
Alcohol -----	4
Monomethylether of ethylene glycol -----	5
Acetic acid ester of monomethylether of ethylene-glycol -----	17

When this lacquer is applied onto a support either with a pencil or, after dilution with other solvents, by means of a spraying pistol, a well sticking, enamel-like lacquer is obtained.

Example 3

A resin having been prepared according to example 2 is melted in vacuo until a test portion of the same is brittle and no longer sticky at 20° C. Then, the resin is dissolved in an excess of hot propanol, freed from small impurities and concentrated so as to form a 70% solution. 7.5 parts of this resin solution are added to a solution of 7.5 parts of acetylcellulose in a mixture of

	Parts
Methylacetate -----	15
Methylalcohol -----	5
Ethylalcohol -----	11.3
Toluene -----	15
1-methoxy-2-acetoxy-ethane -----	35
Diglycolic acid butylene glycolic ester -----	1.7
Phthalic acid ester of monomethylether of ethylene-glycol -----	2

are still added thereto. The clear lacquer thus obtained is applied onto a plate of beechwood, the lacquer for the first coating being preferably somewhat more diluted with the same solvents in order to effect a better penetration of the wood. The lacquer thus obtained is distinguished by a good fastness to weather.

Example 4

100 parts of a 33% formaldehyde-solution are mixed with 7 parts of a 5% ammonia solution so as to assume a pH-value of 7.0. Then 32 parts of phenylurea and 8 parts of the urea from

o-toluidine are dissolved therein at 70-80° C. The water is quickly evaporated by rising the temperature. There remains a light hard resin. This resin is capable of being homogeneously combined with acetylcellulose in the proportion of 3:4. The solution yields clear and hard, practically colorless films having a fastness to water which is better than that of pure acetylcellulose.

Example 5

To 120 parts of formaldehyde there are added 12 parts of a 4% ammonia solution and a mixture of 36 parts of phenylurea with 4 parts of benzenesulfonamide. The mixture is heated until a clear solution is reached, the pH-value being decreased to 5.5-6.0. Then the solution is evaporated in vacuo. The resin being formed at first and having a low melting point is heated until a test portion of the same is brittle at 90-100° C.

A solution of 100 parts of acetylcellulose is capable of taking up 140-150 parts of the resin. Clear, hard and quickly drying films are obtained from this solution.

Example 6

350 parts of a 33% formaldehyde-solution are neutralized with 36 parts of a 5% ammonia solution. 119 parts of phenylurea and 34 parts of o-toluenesulfonamide are dissolved therein at 70-80° C. The water is evaporated in vacuo. The resin is further heated at 90-100° C until it becomes hard. This resin obtained in a yield of 185 parts is almost colorless and compatible with acetylcellulose up to a proportion of 125:100. Hard, very bright and quickly drying lacquers can be obtained therewith.

Example 7

In the same manner as described in the foregoing example, there are condensed with formaldehyde 119 parts of phenylurea in admixture with 15 parts of benzenesulfonamide and 17 parts of p-toluenesulfonamide, 180 g of a colorless resin of the softening point 40° C being obtained thereby. It is compatible up to 200% with acetone-soluble acetylcellulose and yields therewith clear, hard and colorless lacquers. This resin is also compatible for 200% with celluloseacetobutyrate and yields therewith clear, very bright and colorless lacquers of a good fastness to light.

Example 8

1225 parts of a 33% formaldehyde-solution are neutralized with diluted ammonia solution. 332 parts of phenylurea and 165 parts of benzenesulfonamide are dissolved therein by heating. The resin being isolated as described in the foregoing examples has a softening point of 37° C and is compatible for 175% with celluloseacetate as well as with celluloseacetobutyrate.

Example 9

In 350 parts of a formaldehyde-solution being neutralized with diluted ammonia, there are dissolved while heating 82 parts of phenylurea and 63 parts of benzenesulfonamide. The water is evaporated for the most part. Then toluene is added and the mixture is heated while constantly replacing the evaporating toluene until no more water evaporates. The toluene is also distilled off. There remain 160 parts of a hard yellow resin that can be combined for 100% with acetone-soluble celluloseacetate.

GEORG SPIELBERGER.
REINHARDT HEBERMEHL.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR MOTH-PROOFING

Heribert Schüssler, Cologne, Germany; vested in
the Alien Property Custodian

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The present invention relates to a process for protecting any kind of material being liable to the attack by moths and animal pests from the damage caused thereby.

My invention broadly consists in incorporating with the said material a cyclic organic compound containing a nucleus selected from the group consisting of the aromatic and heterocyclic nuclei, and in the said nucleus a substituent containing a quaternary nitrogen atom. In the compounds to be used according to my invention, the said substituent may contain one or more carbon atoms, and the carbon linkage may be interrupted by hetero atoms and/or groups of hetero atoms as, for instance, O, S, SO₂, N, P and the like. Furthermore, the said compounds may be substituted in any desired way, for instance, by halogen, hydroxy, amino, sulfo, sulfoester, carboxylic acid, ether or thioether groups and the like; the compounds may also contain more than one quaternary ammonium group. Besides, I have found such compounds to be particularly suitable for my process as owing to their higher molecular weight have a higher affinity for the material to be protected. Therefore, such compounds are preferably used in my process which contain, as a substituent, an aliphatic radical of at least 6 carbon atoms.

Preferred compounds for use in the process of my invention may be obtained by causing diphenyl derivatives, such as 4-hydroxydiphenyl, to react with monochlorotriethylamine and then transforming the products with monochlorobenzyl chloride into the quaternary ammonium compounds. In this way a substance is obtained which is highly active against textile pests and which possesses an affinity for the fiber. Instead of the 4-hydroxydiphenyl also 4-aminodiphenyl may be caused to react with monochlorotriethylamine in the same manner and transformed as described above into the quaternary compound. The chlorotriethylamine may, for instance, also be replaced by 1,3-monochloropropylamine, and for the subsequent transformation into the quaternary ammonium compound also diethyl sulfate, dimethyl sulfate or other suitable alkylating agents may be used. Instead of monochlorobenzyl chloride also halogenides which are otherwise substituted may be employed.

It is also possible to use instead of diphenyl derivatives, for instance derivatives of diphenylmethane, of triphenylmethane or heterocyclic compounds, as for example:

The condensation product of 1 mol of diethylamino-2'-hydroxy-3'.5'-dichlorodiphenylmethane

and monochlorotriethylamine, rendered quaternary with dimethyl sulfate.

The condensation product of 1 mol of 2,2'-dihydroxy-3,3'.5,5'.4''-pentachlorotriphenylmethane-2''-sulfonic acid sodium salt with 2 mols of monochlorotriethylamine, rendered quaternary with dimethyl sulfate or dichlorobenzyl chloride.

The amides from substituted triphenylmethane sulfonic acids and substituted alkylene diamines which are rendered quaternary on the amine nitrogen atom, as, for instance, an amide from N-methyl-N'-dimethyl (ethyl)-ethylenediamine and rendered quaternary with dimethyl sulfate.

Of the heterocyclic compounds, for instance such of the triphenylmethane type may be mentioned, such as condensation products of isatin with substituted phenols, which compounds are caused to react with monochlorotriethylamine on the nitrogen atom of the isatin and which are rendered quaternary on the amine nitrogen atom.

In a similar manner highly active products can be obtained by causing, for instance, monochlorotriethylamine to react with acid amides and by subsequently rendering quaternary. Also acid chlorides as such may be employed for the same purpose if they are caused to react with such diamines or polyamines as contain at least one N-atom which may be rendered quaternary.

Still another group of products to be used according to my invention are cyclic organic compounds of the general type: R.N^{IV} wherein R is an aralkyl radical and N^{IV} is a quaternary nitrogen atom. Particularly suitable are the aralkyl ammonium compounds substituted in the aryl radical and among these especially the halogen substituted aralkyl-ammonium compounds. Further, the ammonium compounds derived from aralkyl diamines and among these in particular the mono-ammonium compounds which contain one or two aralkyl radicals of the benzene series attached to a tertiary nitrogen atom are particularly effective. If ammonium compounds are used which contain only one nitrogen atom it is advantageous to use such compounds as contain besides the aralkyl radical at least one alkyl radical with 6 or more carbon atoms. The ammonium compounds of the kind specified may be used in the form of the bases or in the form of the salts, in particular in form of mineral acid salts, for instance halides, particularly chlorides, bromides and fluorides, furthermore sulfates and sulfonates and others.

The following substances may be mentioned as mothproofing agents:

Benzyl - diethyl - dodecylammonium chloride, 3,4 - dichlorobenzyl - diethyl - dodecylammonium chloride, xylyl-pyridinium chloride, menaphthyl-pyridinium chloride, bis-(3,4-dichlorobenzyl)-nicotinium chloride, di-(3,4-dichlorobenzyl)-aminoethyl-triethylammonium sulfethylate, (3,4-dichlorobenzyl - methyl) - amino - ethyl - 3',4'-dichlorobenzyl-dimethylammonium sulfomethylate, dibenzyl - dimethyl-di-(3,4-dichlorobenzyl)-trimethylene diammonium bromide.

This series of suitable compounds may be continued at will, in particular on considering what is known about the suitability of the intermediate products as mothproofing agents. For, in the case of such compounds as already in the absence of a quaternary nitrogen atom display a certain protective action against moths, dermestidae and the like, and hinder the growth of bacteria, this protective action is further increased by introducing a quaternary nitrogen atom. The products will then show a sufficient moth-proofing action even in very low concentration. Moreover, compounds of the kind described not only show an affinity for the animal fiber but also for the vegetable fiber and thus are favorably distinguished from such known moth-proofing agents as only take on the animal fiber. This property is of particular importance for the treatment of mixed animal and vegetable material, since it has been found that under certain conditions also vegetable fibers may be attacked by moths and other animal pests.

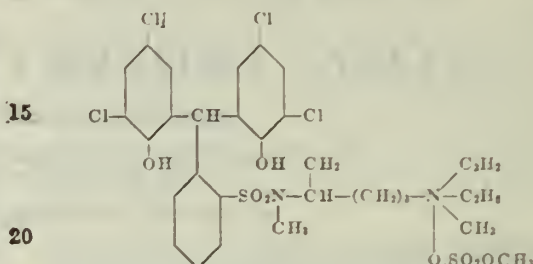
My present process may be used for protecting any kind of material being liable to the attack by moths, dermestidae, bacteria and like animal pests, the said materials comprising for instance textiles, paper, hides, leather, furs, feathers and the like.

My protective substances may be employed in aqueous solution and also in suitable organic solvents. An especially good fixing of the protective substances is obtained by performing the treatment at higher temperatures, for example at boiling temperature. The treatment is preferably combined with one of the usual steps in the treatment of fibrous materials. The treatment may thus take place, for example, during the dyeing or rinsing process, in the back-washing machine, during the finishing or greasing process, or also in French cleaning. Likewise, the solutions of the protective substance may be brought on the fiber by spraying or brushing on or in any way allowing of an even permeation of the material by the protective substance. In many cases it is of advantage to add the protective substance to the soap bath or to use soaps

without, however, restricting it thereto, the parts being by weight:

Example 1

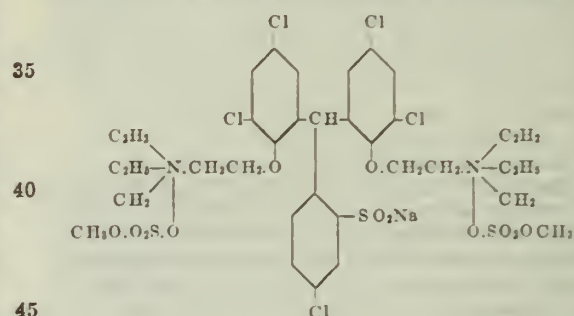
- 5 Wool is treated by boiling for one hour in a dyeing apparatus in a bath of 1:20 with 0.5% of the amide of 3,5,3',5'-tetrachloro-2,2'-dihydroxy-triphenylmethane-2''-sulfonic acid and delta-(methyl-amino-pentyl)-diethyl-methyl-ammonium-sulfomethylate of the formula:



with the addition of 20% of sodium sulfate. The wool is thereby rendered moth-proof.

Example 2

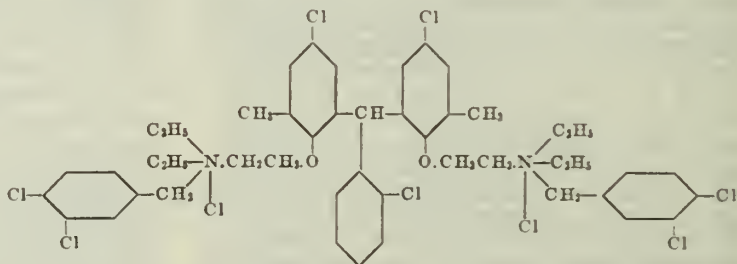
- 25 Mixed tissue of wool and artificial silk from regenerated cellulose is treated for one hour with 2% of the quaternary ammonium compound from 3,5,3',5',4''-pentachloro-2,2'-bis-diethylamino-ethylether - triphenylmethane - 2''-sulfonic acid sodium salt and dimethyl sulfate of the formula:



in a bath of 1:30 at a temperature of 90-95° C. The goods are rendered immune from attack by moth larvae.

Example 3

- 50 Wool yarn is treated for one hour in a bath of 1:50 with 1.5% of the quaternary ammonium compound from 2,2'-diethylaminoethylether-3,3'-dimethyl-5,5',2''-trichlorotriphenylmethane and 55 2 mols of 3,4-dichlorobenzyl chloride of the formula:



at a temperature of 90-95° C. and in the presence of sodium sulfate.

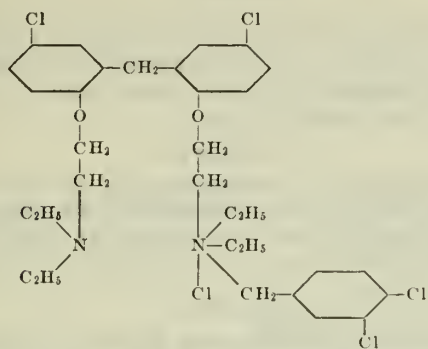
Example 4

Staple fiber from regenerated cellulose is treated for 3 quarters of an hour at boiling temperature with 0.5% of the quaternary ammonium

provided with a content of protective substance. Furthermore, the present products may be used in admixture with each other and with other substances being suitable for combating animal pests like fluorine compounds, alkaloids and others.

The following examples illustrate my invention

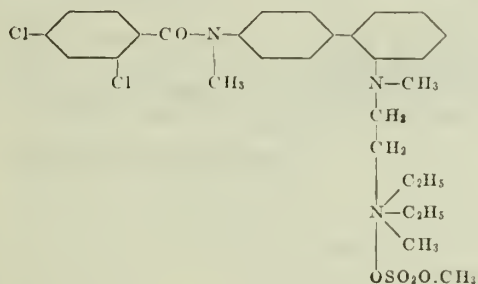
compound of 2,2'-diethylaminoethylether-5,5'-dichloro-diphenyl-methane and 1 mol of 3,4-dichlorobenzyl chloride of the formula:



The goods will not be attacked by moth larvae.

Example 5

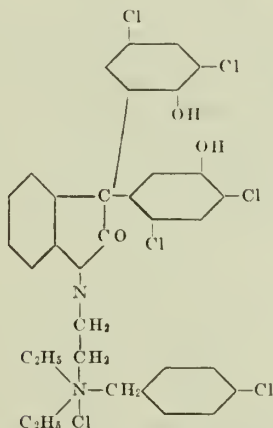
The goods to be treated are immersed in or sprinkled with a 20% alcoholic solution of the quaternary ammonium compound of 2,4-diaminodiphenyl-2,4-dichlorobenzoyl chloride, monochlorotriethylamine and dimethyl sulfate probably of the formula:



The goods are rendered moth-proof.

Example 6

If to a paper pulp 2-3 grams per liter of the quaternary ammonium compound of 3-bis-(3',5'-dichloro-2'-hydroxyphenyl)-1-diethyl-amino-ethyl-oxindol and para-chloro-benzyl chloride of the formula:

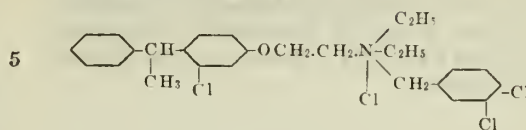


are added the paper produced therefrom is protected against paper pests, such as cockroaches and the like.

Example 7

Wool is treated by boiling for 3 quarters of an hour with 2% of the quaternary ammonium compound from methyl-2-chloro-4-(diethylamino-

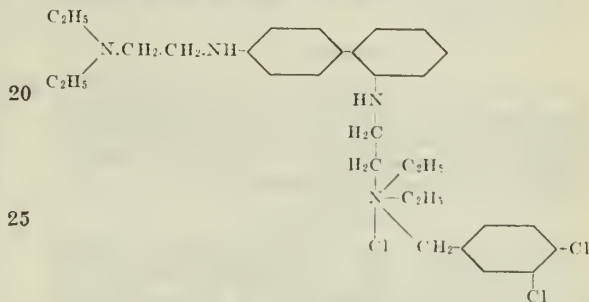
ethoxy)-diphenylmethane and 3,4-dichlorobenzyl chloride of the formula:



The goods are rendered moth-proof thereby.

Example 8

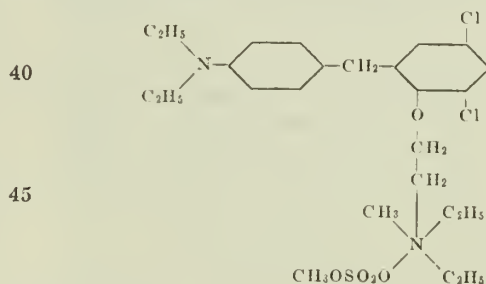
On treating wool by boiling with 1% of the monoquaternary ammonium compound from 1 mol of 2,4-diaminodiphenyl, 2 mols of monochlorotriethylamine and 1 mol of 3,4-dichlorobenzylchloride of the probable formula:



the goods are rendered moth-proof.

Example 9

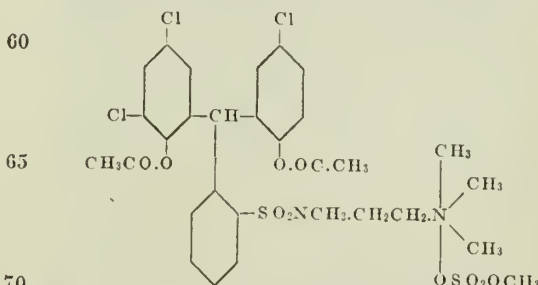
Staple fiber is treated for one hour at 60-70° C with 1.5-2% of the quaternary compound from 4-diethylaminodiphenylmethane-3',5'-dichloro-2'-diethylaminoethyl ether and dimethyl sulfate of the formula:



The goods are rendered immune from attack by moth larvae.

Example 10

Mixed tissue of wool and artificial silk from regenerated cellulose is treated for 3 quarters of an hour at 80° C with 1% of the amide of 3,5,3',5'-tetrachloro-2,2'-diacetoxytriphenylmethane-2''-sulfonic acid and beta-methylaminoethyltrimethylammonium sulfomethylate of the formula:

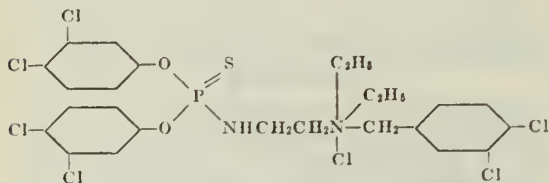


the goods are rendered moth-proof thereby.

Example 11

When treating feathers for half an hour or three quarters of an hour at 30-40° C with a solu-

tion of 6-8 grams per 1 liter of the quaternary ammonium compound being obtainable from 1 mol of 3,4,3',4'-bis(-dichlorophenoxy) phosphor sulfochloride, 1 mol of asymmetric diethylenediamine and 1 mol of 3,4-dichlorobenzyl chloride of the formula:



the feathers are rendered immune from attack by moth larvae.

Example 12

Piece goods are treated on the washing machine in a bath of 1:30 with 3% xylyl-pyridinium chloride for 3 quarters of an hour at 40-50°C and finished in the usual manner. The goods treated in this manner are moth-proof.

Example 13

Wool is treated in a dyeing apparatus in a bath of 1:6 with 1.5% 3,4-dichlorobenzyl-diethyl-dodecylammonium chloride for 3 quarters of an hour at 75°C, centrifuged and dried. The wool thus treated is moth-proof.

Example 14

On adding to an olein spinning softener 10 grams of (3,4-dichlorobenzyl-methyl)-aminoethyl - 3'4' - dichlorobenzyl - dimethylammonium-

sulfomethylate per liter the wool treated with the said softener is rendered moth-proof.

Example 15

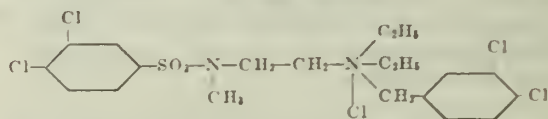
If unspun wool on the backwashing machine is caused to flow in the last bath through a solution 8-10 grams of di-(3,4-dichlorobenzyl)-aminoethyl-triethylammonium-sulfomethylate the wool will not be attacked by moth.

Example 16

On treating wool-covers with a 2-3% solution of menaphthyl-pyridinium-chloride, for instance in chloroform, the wool-covers are protected against moth after the chloroform has evaporated.

Example 17

A woolen fabric is treated for half an hour to 3 quarters of an hour at 60°C in a bath of 1:30 with 1.5% of the reaction product of 3,4-dichlorobenzene sulfomonomethylamide and monochlorotriethylamine which has been transformed by the aid of 3,4-dichlorobenzyl chloride into the quaternary compound of the formula:



Thereby the fabric is rendered immune from attack by moth larvae.

This application is a divisional of our application Ser. No. 161,752, filed August 31, 1937.

HERIBERT SCHÜSSLER.

ALIEN PROPERTY CUSTODIAN

POLYMERIZATION PRODUCTS

Ullrich Hoffmann and Helmut Meis, Marl Kreis
Recklinghausen, Germany; vested in the Alien
Property Custodian

No Drawing. Application filed July 30, 1941

The present invention relates to new polymerization products and to a process of preparing the same. It is known that aromatic vinyl compounds such as styrene if subjected to the action of heat or of polymerization catalysts are converted into high molecular products of a chain-like structure. In case the polymerization of such aromatic vinyl compounds is effected in the presence of other polymerizable or copolymerizable compounds there are obtained mixed polymerizates containing both types of starting materials in any desired proportion and alteration. Now, the US. Patent 2,224,837 to Leo Rosenthal and one of us has taught that a new type of polymerizates can be prepared by causing acid reacting polymerization catalysts to react upon a mixture of aromatic vinyl compounds with aromatic hydroxy compounds and/or alkyl ethers thereof. From the French Patent No. 69,620 (Patent of addition to No. 804,891) it follows that similar products can be obtained by employing as catalysts the so-called bleaching earths such as "fuller's earth". Depending on the conditions of working and on the proportions of the starting materials the polymeric products thus obtained represent viscous difficultly volatile oils or solid substances of a resin-like character. The outstanding feature of most of the resin-like products of the character described is their being soluble in the usual lacquer benzene, in the oil of turpentine and in drying or non drying oils. Part of the said polymerization products are even capable of being homogeneously combined with polymerized oils. In these respects, the said new products are clearly differentiated from the hitherto known polymerized aromatic vinyl compounds and from mixed polymerizates containing the same. Hence follows that the said new products can be employed as additional substances for the preparation of lacquers such as oil varnishes and so on. Moreover, the said new products are capable of reacting with formaldehyde, new condensation products of an increased molecular weight being obtained thereby.

In accordance with the present invention aromatic vinyl compounds, i. e. aromatic compounds which are substituted by the radical $\text{CH}_2=\text{CH}-$ are capable of being converted into new polymerization products which in chemical structure and in physical behaviour resemble those of the U. S. Patent 2,224,837 mentioned above by subjecting the same in the absence of water to the action of acid reacting polymerization catalysts in the presence of such aldehydes or ketones as have the carbonyl group conjugated with a C—C

double linkage. In accordance with what is stated in the French patent mentioned above the acid reacting catalyst can be replaced by bleaching earths such as fuller's earth. Examples for suitable aromatic vinyl compounds are styrene, vinyl naphthalene, divinyl benzene and vinyl anisol. As aldehydes or ketones of the character described there can be employed vinyl methyl ketone, crotonaldehyde, cinnamic aldehyde, benzaldehyde, acetophenone and benzoquinone, it being to be understood that the unsaturated C—C double linkage which must be conjugated with the carbonyl group may be of an aliphatic or aromatic nature. Attention is directed to the fact that part of the said aldehydes, such as vinyl methyl ketone, are capable of being polymerized whereas others such as benzaldehyde are not. Under the influence of the catalysts described these products in admixture with the aromatic vinyl compounds are converted into polymeric products which are believed to contain a chain of the usual polystyrene type, the aldehydes or ketones representing the terminal members thereof. In accordance therewith the molecular weight of our new polymerization products increases with a decrease of the proportion of the aldehydes or ketones, there being practically no lower limit for the latter. On the other hand, the aldehydes and ketones are not capable of reacting with the aromatic vinyl compounds in a higher proportion than that corresponding to one carbonyl group per each one vinyl group. In case a higher proportion of aldehydes or ketones of the character described is employed, the aqueous aldehydes and ketones can be recovered for the most part in an unchanged state.

The reaction is preferably carried out in the presence of an indifferent solvent such as carbon-tetrachloride, benzene or toluene. Depending on the starting materials and on the catalysts employed the reaction mixture must be heated or heat is evolved during reaction so that the mixture must be cooled. As catalysts there can be employed for instance tinteirachloride, ferric chloride or borofluoroacetic acid. Generally spoken, all acid reacting polymerization catalysts are suitable for the purpose in question. The reaction being finished the catalyst can be removed by treating the reaction mixture with water or with alkali or earth alkali metal oxides, hydroxides or carbonates. In case bleaching earths are employed as catalysts the reaction mixture can be worked up by removing the same by filtration.

Depending on the nature and the proportion of the starting materials our new products can be

employed for various purposes. The high molecular products, i.e. those containing in chemical combination a relatively low proportion of aldehydes or ketones of the character described can be employed as such or as additional substances for the preparation of lacquers, oil varnishes and the like. In general, such products should not contain less than one carbonyl group per about 100 vinyl groups. Low molecular polymerizates, i.e. those containing in chemical combination a relatively high proportion of aldehydes and ketones of the character described can partially be employed for similar purposes. Others can be employed as starting materials for other reactions, for instance for reaction with formaldehyde, valuable products of an increased molecular weight being obtained thereby.

As a matter of fact, there can also be employed mixtures of various aromatic vinyl compounds and/or mixtures of various aldehydes and/or ketones of the character described as well as mixtures of such aldehydes and/or ketones with phenols or phenol ethers, i. e. the starting materials of the US Patent 2,224,837.

The following examples illustrate the invention without restricting it thereto, the parts being by weight:

Example 1

A mixture of 208 parts of styrol and 140 parts of crotonaldehyde is diluted with 400 parts of xylene. To the said mixture there is gradually added such an amount of borofluoroacetic acid as is sufficient to effect an increase of temperature. Then the temperature is kept at 40°C by gradually adding further amounts of catalyst. When by the addition of catalysts no increase of temperature is observed any longer, the mixture is stirred for a short time to 100°C. Thereupon the borofluoroacetic acid is neutralized by adding ground soda to the reaction mixture. After filtration the clear solution is freed from the solvent and smaller quantities of highly boiling ingredients. There remain 340 parts of a resin which is viscous in the heat and solid at room temperature and is soluble in benzene, toluene, carbon tetrachloride, xylene, acetone and linseed oil.

Example 2

To 104 parts of styrene and 105 parts of benzaldehyde in 200 parts of xylene there are gradually added at a temperature of about 30 to 40°C 30 parts of borofluoroacetic acid. By suitable cooling the reaction temperature is kept within these limits. The reaction being finished the solution is treated with a mixture of calcium oxide and soda, until a test portion which has been filtrated and shaken with water does not show any longer an acid reaction in the aqueous layer. Thereupon the filtrated solution is worked up as described in example 1. There are obtained 205 parts of a light yellow resin which is soluble in benzene, toluene, xylene, acetone, carbon tetrachloride and linseed oil. It is insoluble in alcohol.

Example 3

104 parts of styrene and 11 parts of benzaldehyde are diluted with 200 parts of xylene and condensed by gradually adding thereto borofluoroacetic acid. By working up as described in the foregoing examples there are obtained 114 parts of a nearly colorless resin which is soluble in linseed oil even at a temperature of 0°C.

Example 4

104 parts of styrene and 60 parts of acetophenone are diluted with 200 parts of xylene and gradually mixed with 15 parts of tin tetrachloride at a temperature of between 20 and 40°C. The reaction being finished the mixture is stirred for several hours and then the catalyst is removed by treating the reaction mixture with a mixture of sodium and calcium carbonate. There remain 130 parts of a soft resin.

Example 5

In the presence of 200 parts of xylene there are caused to react with each other 104 parts of styrene and 20 parts of benzoquinone by gradually adding thereto 25 parts of borofluoroacetic acid within 1½ hours at a temperature of 40°C. The catalyst is removed by stirring with soda and filtration. After evaporation of the solvent and of a small amount of high-boiling condensates there remains a resin which is soluble in benzene, carbon tetrachloride, xylene, toluene and linseed oil.

Example 6

200 parts of xylene are diluted with 100 parts of styrene and 100 parts of acetophenone, whereupon 40 parts of borofluoroacetic acid are added thereto within 1½ hours. The reaction being finished the mixture is stirred for 8 hours at 90°C. The catalyst is removed as described in one of the foregoing examples and the filtrated reaction is heated in vacuo until at 10 mm and 210°C there is no evaporation any longer. There remain 160 parts of an oil which is very viscous at room temperature.

Example 7

50 parts of fuller's earth are heated with a mixture of 100 parts of styrene, 70 parts of benzaldehyde and 200 parts of xylene for 8 hours at a temperature of 90–100°C. After cooling the fuller's earth is filtered off and the solution evaporated. After removal of the solvent, the non-reacted substance and a small amount of high-boiling condensation products there remain 14 parts of a viscous oil which is miscible with benzene, toluene, xylene and linseed oil.

Example 8

104 parts of styrene and 63 parts of α -ethyl- β -propyl acrolein are gradually mixed with 300 parts of carbon tetrachloride and 30 parts of borofluoroacetic acid and then the mixture is stirred for several hours at 70°C. Thereupon the reaction mixture is cooled and neutralized with 50 parts of soda at room temperature while stirring. After filtration the solution is freed from the solvent by distillation. There remain 160 parts of a sticky and soft resin.

Example 9

100 parts of styrene and 13 parts of cinnamic aldehyde in 200 parts of toluene are condensed with borofluoroacetic acid at 40°C. After neutralization, filtration and removing of the solvent and of high-boiling condensation products there is obtained a yield of 110 parts of a light yellow hard resin which is soluble in linseed oil, benzene and carbon tetrachloride.

Example 10

A solution of 104 parts of styrene, 50 parts of benzaldehyde and 25 parts of acetophenone in 200 parts of xylene is condensed with 20 parts of borofluoroacetic acid at 40°C. By stirring at

room temperature with a mixture of calcium oxide and calcium carbonate the reaction mixture is neutralized. After filtration the solvent is distilled off and the remainder is heated to 210° at 10 mm pressure. There remain 165 parts of a light yellow resin which is very hard.

Example 11

Into a mixture of 100 parts of divinyl benzene, 50 parts of benzaldehyde and 200 parts of benzene there are gradually added 20 parts of borofluoracetic acid. Thereupon the mixture is heated to boiling for about 3 hours. Then the catalyst is neutralized by digesting the mixture with free calcium oxide. After filtration and after evaporation of the solvent in vacuo there are obtained 145 parts of a light colored resin, which is soluble in benzene, xylene, toluene and in linseed oil.

Example 12

Into a mixture of 200 parts of styrene, 10 parts of phenol, 20 parts of acetophenone and 200 parts of benzene there are gradually added 5 parts of borofluoracetic acid. Then the mixture is heated to boiling for several hours, whereupon the catalyst is neutralized as described in the foregoing example and the solvent is evaporated. There are obtained 200 parts of a light colored resin of the softening point: 86°C, which is soluble in linseed oil.

Example 13

In case in example 12 the phenol is replaced by 11 parts of phenoxyethanol, there are obtained 220 parts of a light colored resin which is soluble in linseed oil and shows the softening point: 80°C.

Example 14

Into a mixture of 104 parts of styrene, 10 parts of benzaldehyde, 1 parts of acetophenone and 200 parts of toluene there are gradually added 10 parts of borofluoracetic acid. The reaction being finished the mixture is stirred for a short time at 80°C, whereupon the catalyst is neutralized. After filtration and evaporation of the solvent there are obtained 121 parts of a light colored resin of the softening point: 83°C.

Example 15

Into a solution of 104 parts of styrene, 10 parts of benzaldehyde, 10 parts of acetophenone and 200 parts of xylene there are added at 90°C while stirring 40 parts of an active aluminium hydroxide. The reaction being finished the mixture is stirred for several hours at 100°C. After filtration and removal of the solvent there are obtained 120 parts of a soft resin with a softening point of below 60°C.

Example 16

A mixture of 15.8 parts of β -naphthoquinone and 104 parts of styrene is diluted with such an amount of benzene as to yield a solution which is clear at 40°C. At this temperature there are added 4 parts of borofluoracetic acid, whereupon the mixture is heated for 3 hours at 40°C. After neutralization by means of 40 parts of water-free sodium carbonate and after the addition of 10 parts of a bleaching earth the mixture is filtered and the solvent is evaporated. There are obtained 100 parts of a brownish colored hard resin.

ULLRICH HOFFMAN.
HELMUT MEIS.

ALIEN PROPERTY CUSTODIAN

PROCESS OF PREPARING KETENE

Bernhard Popp, Frankfurt am Main, and Walter Johannes Ostrowski, deceased, late of Frankfurt am Main, Germany, by Else Marie Emma Ostrowski, Frankfurt am Main, Germany, widow and guardian of Jorg Ulrich Ostrowski, sole heirs; vested in the Alien Property Custodian

Application filed July 30, 1941

It is known that ketene may be prepared by heating acetic acid or acetic anhydride to high temperatures under reduced pressure in the presence of catalysts splitting off water, cf., for instance, Patent No. 2,108,829. Directly after leaving the tube, the cleavage gases are preferably cooled or sucked through water of 0°C whereby the unchanged acetic acid is removed. In view of the great velocity of flow the ketene practically does not react with the water. In order to isolate the ketene which is rarefied by other gases such as CO, CO₂, ethylene or the like it was necessary, hitherto, to condense the ketene, which boils at -41°C under a pressure of 760 mm, on the vacuum-side in receivers cooled by means of liquefied air. This process is uneconomical and its carrying out on an industrial scale is complicated and difficult. On the other hand, it has not been possible hitherto to isolate on a mass scale the ketene on the pressure-side of the vacuum pump.

Now, we have found that the above problem may be solved by cooling the vacuum pump to temperatures as low as possible, using a lubricant which is indifferent against ketene and has a viscosity sufficient for the temperatures in question and, thereupon, isolating the ketene on the pressure-side or working it up without isolation.

Advantageously vacuum pumps are used which have very small lubricating surfaces and may be cooled to temperatures from about 0°C to about -30°C. For this purpose it is advisable to apply an external cooling from about -60°C to about -70°C. As lubricating agents there are used indifferent oils, for instance, higher saturated hydrocarbons which still show a suitable lubricating-consistency at temperatures ranging as much as possible below 0°C and do not react with, or change the ketene, for instance paraffin oil having a viscosity of ζ -16=494.05, furthermore vaseline oil, indifferent mineral oils in general, as well as decahydronaphthalene, tetrahydronaphthalene.

It is advisable to provide for a continuous lubrication in order to remove the impurities which accumulate in the pump and which consist mainly of acetic anhydride. An accumulation of the impurities may very detrimentally affect the output of the vacuum pump already after a short time (about 24 hours). The impurities consisting mainly of acetic anhydride are due to the acetic acid vapors not split up and taken along by the carrier gases, which vapors easily react with ketene, especially above 0°C, with formation of acetic anhydride.

The splitting up of acetic acid or acetic anhydride may be performed in known manner, for instance, according to Patent No. 2,108,829. A pressure of about 2 to about 200 mm may be applied and temperatures of between about 400°C and about 900°C, advantageously between about 600°C and about 800°C may be used. As catalysts there are suitable, for instance: phosphorus compounds such as triethylphosphate; furthermore, volatile nitrogen compounds such as ammonia, pyridine, methylamine and phenylamine may be present.

The present process allows of isolating ketene in an economical manner or of further working it up, without previous isolation, into other products of industrial importance.

The following example illustrates the invention:

Gases containing ketene and obtained by dissociation of acetic anhydride are freed from water and acetic acid and introduced into a vacuum pump. The pump is a centrifugal piston pump with an output of 4 cbm per hour and is illustrated in the accompanying drawing, Figs. 1 and 2, as follows: the pump is provided with a cooling jacket 1, an exhaust pipe 2, a screw 3 for controlling the oil level, a suction pipe 4, a screw 5 for regulating the vacuum, a screw 6 for drawing off the oil, a valve 7, an oil supply 8 and an oil collector 9 for drawing off the oil. During the working, an inner temperature up to -20°C is maintained. The lubricant is introduced continuously through suction branch 4. As lubricant there is used paraffin oil having a viscosity of ζ -16=494.05. Through the bore for screw 3 serving for the control of the oil surface the impurities formed which mainly consist of acetic anhydride besides traces of resinifications are collected. The continuous lubrication which at the same time serves as a cleaning means for the pump amounts to 200 cc. in 24 hours. The acetic anhydride in the collected paraffin oil separates easily and the paraffin oil may be used again without being purified. The acetic anhydride formed in the pump amounts to 0.2% (including resinification). In a fortnight's continuous working the pump transfers 99.5% of the ketene from the vacuum-side to the pressure-side at a pressure of 15-20 mm.

As vacuum pump there may be used in a corresponding manner a slide valve pump with an output of 240 cbm per hour. The oiler pumps the paraffin oil as lubricant into the gliding surfaces cooled by means of a cooling lye. The paraffin

oil contaminated with acetic anhydride is removed by separators arranged in the exhaust.

Instead of providing the pump with a cooling jacket it may also be cooled internally, for instance, by conducting in cycle an indifferent liquid which does not dissolve ketene, such as, paraffin oil, through the pump and a cooler mounted outside the pump.

It is possible by means of a two-stage turbine pump or an "Elmo"-pump to force deeply cooled 10 decahydronaphthalene at a pressure of about 4 atmospheres above atmospheric pressure in cycle

by means of water jet pumps into a vessel which may be cooled. The cooling is effected, for instance, by a mixture of carbonic acid and butanol. The water jet pumps produce a pressure of 15 mm. On the suction side of the water jet pumps the ketene is sucked and on the pressure side of the cooling vessel it is discharged.

BERNHARD POPP.

ELSE MARIE EMMA OSTROWSKI,

*As administratrix of Walter Johannes Ostrowski,
Deceased.*

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BY A. P. C.

B. POPP ET AL
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Fig. 1

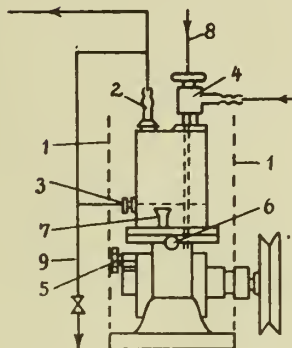
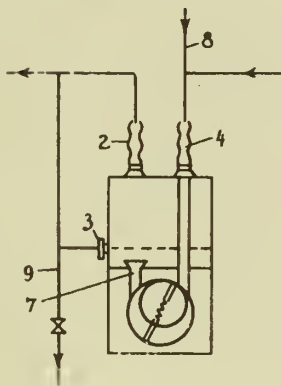


Fig. 2



Bernhard Popp
Walter Johannes Ostrowski
INVENTORS

BY *Hubert J. Joslin*
THEIR ATTORNEYS

ALIEN PROPERTY CUSTODIAN

PREPARATION OF ORGANIC DIISOCYANATES

Heinrich Rinke, Leverkusen-Schlebusch, 2, and
Karl Taube, Leverkusen-I. G. Werk, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed August 8, 1941

The present invention relates to a new process for preparing organic diisocyanates.

Up to the present, organic diisocyanates have been prepared by causing phosgene to react upon diamine dichlorohydrates in the presence of an indifferent organic solvent at an elevated temperature care being taken that the hydrogen chloride evolved is quickly removed from the reaction mixture. The said reaction proceeds relatively slowly as the dichlorohydrates are practically insoluble in organic solvents.

It is the object of our present invention, to do away with these disadvantages and to develop a new process, which allows one to prepare organic diisocyanates in an easy and economical manner.

With this and other objects in view our invention comprises the combination of the following steps:

- (a) we are starting from free diamines,
- (b) these diamines are added into a solution of phosgene in an indifferent solvent at a temperature at which no evolution of hydrogen chloride occurs;
- (c) thereupon the temperature is raised to a point at which hydrogen chloride is split off,

care being taken, that the amount of phosgene during step b is at least 1 mol per each mol of diamine and that during step c the amount of phosgen is at least about 2 mols per each mol of diamine, including that amount of phosgene, which has been consumed during step b. In accordance with a special method of working the amount of phosgene is at least about 2 mols from the very beginning so that the introduction into the reaction mixture of additional phosgene during step c can be dispensed with.

It is believed, that in the course of step b there is formed a chlorohydrate of the amino-carbamic acid chloride of the diamine employed. This intermediate product separates out from the solution and is converted by the additional phosgene during step c into the diisocyanate, hydrogen chloride being split off. As a matter of fact, the chlorohydrate separating out during step b can be isolated from the reaction-mixture prior to the performing of step c.

Our new process can be employed for the preparation of various diisocyanates, for instance of those of the aliphatic or aromatic series. The carbon chains may also contain hetero atoms such as sulphur or oxygen. Suitable indifferent solvents are aromatic hydrocarbons and the alkyl and halogen substitution products such as toluene

or dichlorobenzene. During step b the reaction mixture is preferably kept at a temperature below about 10°C whereas during step c a higher temperature of up to about 200°C is preferred. In practice we are working at a temperature between about 140—about 170° C. At the end of the reaction a stream of an indifferent gas may be passed through the solution in order to remove excess hydrogen chloride and excess phosgene. This is the more advisable as we prefer to work with an excess of phosgene during step b as well as during step c.

The following examples illustrate the invention without however restricting it thereto the parts being by weight:

Example 1

Into a solution of 120 parts of phosgene in 500 parts of o-dichlorobenzene there is added a solution of 116 parts of hexamethylenediamine in 500 parts of o-dichlorobenzene drop by drop while well cooling and stirring at a temperature of not more than +5°. Immediately the monochlorohydrate of the 1-aminohexamethylene carbamic acid chloride is separated. While stirring quickly the suspension is heated to 150–160°; within 7–8 hours 400 parts of phosgen are added. Hexamethylene diisocyanate is formed by the splitting off of hydrochloric acid. After the evaporating of the o-dichlorobenzene, the hexamethylenediisocyanate is distilled under 10mm at 124°. It is obtained in a yield of more than 80%.

Example 2

Into a solution of 30 parts of phosgene in 110 parts of o-dichlorobenzene there is added a solution of 50 parts of the mixture of undekamethylene- and dodekamethylenediamine (1:1) in 200 parts of o-dichlorobenzene while stirring and cooling. While adding further 240 parts of phosgene the suspension of the chlorohydrate carbamic acid chloride is heated for 4 hours to 150°. The precipitate having been dissolved and the solvent having been distilled off the mixture of the undekamethylene and dodekamethylene-diisocyanate is obtained in a yield of more than 90%. $Kp_{10}=168-182^{\circ}$.

Example 3

Into a solution of 60 parts of phosgene in 220 parts of o-dichlorobenzene there is added a solution of 67 parts of 1,3-diaminocyclohexane in 400 parts of o-dichlorobenzene while stirring and cooling. Then the suspension formed is heated to 150–160°, kept at this temperature for 8–9 hours

and meanwhile 300 parts of phosgene are added. After removal of the solvent by distillation hexahydro-*m*-phenylenediisocyanate of the boiling-point 89° is obtained at 1.8 mm in a good yield.

Example 4

The hot solution of 244 parts of dianisidine in 900 parts of *o*-dichlorobenzene is added while cooling to a solution of 120 parts of phosgen in 450 parts of *o*-dichlorobenzene. Then 110° parts of phosgene are added while heating to 150–160°. The still hot solution is treated with animal charcoal, heated and sucked off. The 3.3'-diethoxydiphenyl-4.4'-diisocyanata separates in a crystallized state. (Fp. 121–122°).

Example 5

The solution of 50 parts of 3.3'-diaminodi-

propylether in 260 parts of *o*-dichlorobenzene is poured into a solution of 50 parts of phosgene in 130 parts of *o*-dichlorobenzene at a temperature of below 0°. After the heating up to 50° the carbamic acid chloridechlorohydrate which has been precipitated in the cold is dissolved. At 130° after the adding of further phosgene hydrochloric acid is split off, whereupon the 3.3'-diisocyanate-dipropylether, which boils at 102–104° at 2.6mm is formed. The diisocyanate is a waterlight liquor having a sharp smell. Upon adding aniline while heating strongly it formes the 3.3'-bis-(*ω*-phenylureido)-dipropylether which melts at a temperature of 177–179°.

15

HEINRICH RINKE.
KARL TAUBE.

ALIEN PROPERTY CUSTODIAN

METHOD OF CONCENTRATING LATEX

Godfried Johan Van Der Bic, Buitenzorg, Java,
Netherlands East Indies; vested in the Alien
Property Custodian

No Drawing. Application filed August 12, 1941

This invention relates to method of concentrating latex; and it comprises a process in which there is added to a latex to be concentrated a stabilizing or peptizing agent, usually in small quantity but sufficient to produce a stability of not substantially less than about 15 minutes, as determined by the Hamilton Beach Stirrer test, without substantially increasing the viscosity of the latex, and the latex is then passed through a centrifuge adjusted to produce a concentrated cream having a rubber content of over 60 per cent by weight; all as more fully hereinafter set forth and as claimed.

It has long been known that aqueous rubber dispersions especially rubber latex, can be separated into two layers of differing rubber content by means of centrifugal action. The upper layer obtained is richer and the lower layer is poorer in rubber constituents than the starting dispersions. But according to this method it is only possible to obtain a cream with a rubber content of about 60 per cent. The same can be said of creams obtained by creaming with the aid of a mucilaginous substance.

C. F. Flint comments on these limitations in processes of concentrating latex in his book entitled "Chemistry and Technology of Rubber Latex" (1938). On page 200 he states, for example: "In a latex of 60 per cent rubber content the particles are already so closely packed that their freedom of movement in the serum is restricted by their proximity one to another. The viscosity of a 60 per cent latex limits to a cream of this rubber content the separation that can be achieved by centrifuges of practicable speed."

Further on, page 209, he states: "It will be noted that in creaming as in centrifuging a rubber content of 60 per cent is approximately the upper limit of concentration."

The present invention relates to a process for the concentration of aqueous rubber dispersions by centrifugal action, wherein a substance is added to the dispersion before concentration, which substance increases the mechanical stability of the aqueous rubber dispersion. The increase of the mechanical stability in this manner makes it possible to obtain a cream with a rubber content of more than 65 per cent in a normal centrifugal machine without any difficulties arising. This is a new result in the rubber art.

Care must be taken that the added substances, which increase the mechanical stability, do not bring about any considerable increase of viscosity of the rubber dispersion. The materials which are operative are those which are usually classified as peptizing or emulsifying agents, and which tend to reduce the viscosity while increasing the stability, apparently due to an increase in the degree of dispersion of the rubber particles. These substances are to be contrasted with the so-called protective colloids which increase stability primarily through an increase in viscosity. Alkali metal soaps, for example, are particularly effective, while protective colloids such as haemoglobin and mucilaginous substances, are ineffective. It is also necessary that the substance added be capable of producing a certain minimum increase in mechanical stability.

It has been found that there is a critical stability value above which it is possible to obtain increased rubber concentrations in the centrifuging process and below which the improvement obtained is not appreciable. This stability value is of the order of 15 minutes, as determined by the standard method in which a Hamilton Beach Stirrer operating at a rate of 10,000 revolutions per minute is employed. If this stirrer can be operated in the latex for a period of 15 minutes or over without the formation of irreversible flocculated particles, the latex has the required stability. All peptizing, dispersing or stabilizing agents which are compatible with latex and which are capable of producing this stability, without appreciably increasing the viscosity of the latex, are suitable for use in the present process. The number of agents which are capable of producing this desired stability are rather few.

The addition of various stabilizers to latex is, of course, very old. But it has apparently never been discovered heretofore that the addition of certain of these stabilizers, in quantity sufficient to produce a stability above a certain critical value, enables the production of creams having rubber concentrations of over 60 per cent merely by passing the treated latex through a properly adjusted centrifuge.

The present invention also includes the discovery that the treated latex can be passed through a centrifuge without stoppage for a time which is at least twice as long as that in the case

of an untreated latex. This feature, of course, greatly extends the capacity of the centrifuging plant. A further incidental advantage of the new process is that the creams produced are more stable than those produced by centrifuging untreated latex owing to the fact that part of the stabilizing agent remains in the cream after the centrifugal action.

A large number of stabilizing agents have been examined, using the Hamilton Beach Stirrer test, in order to determine their effectiveness. Part of the results obtained are collected in the following table:

Addition per liter latex	Mechanical stability
No addition (latex with a content of 32% of rubber and 0.3% of ammonia)	2' to 2'30"
3 g. ammonia	2' to 2'30"
50 ml. NaOH 5%	4' to 4'30"
50 ml. soda 5%	2'30" to 3'
50 ml. borax 5%	2'30" to 3'
25 ml. borax casein 10%	3' to 3'30"
50 ml. borax casein 10%	4' to 10'
50 ml. Vultamol 5%	2' to 2'30"
50 ml. Nekal BK (an alkyl naphthalene sulfonate) 5%	9' to 10'
25 ml. Igepon (acid sulfuric ester of octodecyl lactate) 5%	3'30" to 4'
50 ml. Igepon (acid sulfuric ester of octodecyl lactate) 5%	6' to 7'
50 ml. Turkey red oil 5%	3'30" to 4'
50 ml. Vulestap N 5%	7' to 8'
25 ml. sodium soap solution 5%	12' to 13'
50 ml. sodium soap solution 5%	30'
10 ml. borax-casein 10% + 15 ml. Igepon 5%	6' to 7'
10 ml. borax-casein 10% + 25 ml. soap 5%	24'
10 ml. Igepon 5% + 25 ml. soap 5%	24'

As stated above only those stabilizers are suitable which are capable of bringing the mechanical stability of rubber dispersions to at least 15'. Of the various agents listed in the table, 50 ml. 5% sodium soap solution, 25 ml. of 5% soap solution mixed with 10 ml. of 10% borax-casein, and 25 ml. of soap solution mixed with 10 ml. of 5% Igepon are thus seen to be suitable. The addition agent may be added immediately before or during the centrifugal action.

The invention can be explained with somewhat greater particularity by reference to the following specific examples which represent illustrative as well as practical embodiments of the improved process.

Example 1

The latex employed in this example contained 32.1% of rubber and 0.25% ammonia. It was purified before treatment by settling for 20 hours. The test was made two days after tapping. The centrifuge employed was one of the usual De Laval type, bowl type L770, operating at about 7000 revolutions per minute.

Part of the latex was concentrated without the addition of a stabilizer and the bowl was found to be obstructed after 110 minutes. The rubber content of the cream was found to be 61 to 62% and of the serum (the under latex) 8 to 9.5%. The average capacity was 210 kg. latex (32.1%) per hour.

To another part of the same latex 50 ml. stabilizing solution per liter were added. This stabilizing solution consisted of 5 per cent solution of sodium soap and Igepon in a proportion of 5 to 2. This treated latex was then centrifuged with the same adjustment of the centrifugal machine operating at the same number of revolutions per minute. The operation was stopped after 5½ hours at which time no obstruction of the bowl had occurred. When the bowl was opened its condition appeared to be such that it

would have been possible to have continued the operation for several hours longer.

The rubber content of the cream was found to be 63 to 64 per cent and of the under latex 8 to 9 per cent. The average capacity was 190 kg. latex (32.1%) per hour.

For the mechanical stability the following values were found:

	Without stabilizer	With stabilizer
Starting latex	Minutes 2	Minutes 60
Cream	1 to 3	7 to 8

This example shows that, by the addition of a stabilizer improving the mechanical stability, a more concentrated cream can be obtained with a greater mechanical stability, using the same adjustment of the centrifuge, and that the centrifugal can be used for a longer time without obstruction occurring.

Example 2

The latex employed in this example contained 32.6% rubber and 0.35% of ammonia. The greater part of the heavy impurities was removed by settling for 40 hours.

The test was conducted on the second day after tapping with the aid of the same centrifuge as that used in Example 1, operating at the same speed. But the adjustment of the centrifuge was changed to produce a more concentrated cream.

With the new adjustment of the centrifuge, it was attempted to concentrate the untreated latex but it was found that stoppage of the bowl occurred almost at once so that no practical results could be obtained. Another sample of latex was then centrifuged which had been stabilized by the addition of the same stabilizer and in the same quantity as that used in Example 1. In this test a cream was obtained having a rubber content of 64.8 to 65.8%, while the rubber content of the under latex or heavier fraction was found to be 8.6 to 8.9%.

The following values for the mechanical stability were found:

Starting latex	10'
Starting latex with stabilizer	55'
Cream	10' to 11'

The treated latex was passed through the centrifuge for a period of 1 hour with a capacity of 150 kg. latex per hour. During this period there was no observable clogging or obstruction of the bowl.

This example shows that the treated latex of the present invention can be centrifuged under conditions of adjustment which cannot be employed with an untreated latex, and that the latex thus obtained has a rubber content and stability which are substantially higher than those obtainable using an untreated latex.

While several of the more advantageous embodiments of the new process have been described, it is evident that various modifications can be made in the specific procedures which have been set out without departing from the purview of this invention. It is possible to realize the benefits of this invention with any of the so-called high speed types of centrifuges which are capable of use in the usual procedure of centrifuging latex. The adjustment of the centrifuge can be altered to increase the concen-

tration of the latex cream somewhat above 65% but, of course, this can be done only at the expense of capacity and of shorter operating runs. In general it may be said that, the higher the stability of the treated latex, the more concentrated the resulting cream which can be obtained. The cost of the stabilizing agent and the contamination of the latex caused thereby are two of the factors which produce an upper limit to the concentrations which can be obtained 10

in practical operation. While it has been stated that any peptizing or stabilizing agent can be used which is capable of producing a stability of 15 minutes, it is obvious, of course, that in practical operations the only agents of this type which are useful are those capable of producing this required stability when added to the latex in relatively small proportions, such as 1 per cent or less.

GODFRIED JOHAN VAN DER BIE

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF PURIFIED RUBBER

Godfried John van der Bie, Buitenzorg, Java,
Netherlands East Indies; vested in the Alien
Property Custodian

No Drawing. Application filed August 16, 1941

This invention relates to manufacture of purified rubber; and it comprises a process wherein a water-soluble, metal-complex-forming reagent, such as an alkali metal cyanide, is added to an aqueous dispersion of rubber, whereby any insoluble metal compounds present are converted into soluble metal complexes, followed by separation of the aqueous phase, including said soluble metal complexes, from the rubber. The invention also includes the purified rubber resulting from the said process, having a content of copper, for example, not substantially exceeding 0.2 to 0.25 mg. per 100 grams of rubber; all as more fully hereinafter set forth and as claimed.

It is known that small amounts of metal compounds, such as copper, manganese and iron, exert a detrimental influence on the durability of raw or vulcanized rubber. Accordingly in practice, a limit has been set for the permissible amount of each of these metals. Furthermore it is known that in rubber dispersions small amounts of compounds of the above mentioned metals occur. Some natural latices may even contain relatively high copper contents.

The metal compounds present in latex are usually partly in the dissolved and partly in an undissolved condition. In the undissolved condition these compounds are adsorbed on the rubber particles or are present in flocculated form, suspended in the serum or precipitated on or in the rubber particles.

The object of the present invention is to solubilize and remove insoluble detrimental metal compounds of this type occurring in rubber, especially in rubber dispersions. The term rubber includes rubber of *Hevea brasiliensis*, gutta-percha, balata, djelutong, abiurana and knodang throughout the following description and in the claims.

When dispersions of rubber are coagulated about half of the metal content present goes into the serum, the other half remaining in the rubber. The metal compounds, especially the copper compounds, exert a detrimental influence on the aging properties of the rubber, which detrimental influence can be partly neutralized or reduced by substances occurring in natural rubber dispersions that is, by the so-called anti-oxidants, which protect the rubber against depolymerization and oxidation. But purified rubber, for example, rubber used for electrical purposes is generally free from these anti-oxidants owing to their removal during purification. The detrimental influence of the prejudicial metal compounds is therefore greatly enhanced.

In those methods of purifying latex which involve boiling of the latex with an alkali, the metal compounds present are nearly completely converted, during the resulting hydrolysis, into compounds which form insoluble combinations when the latex is coagulated. In these methods therefore a substantial part of the metals, such as copper, which are present in the original latex, remain in the purified rubber. It is probable that in some cases the copper is precipitated in the form of sulfidic compounds, by reaction with the sulfur ions formed by hydrolysis of the non-rubber constituents present.

In order to produce a durable rubber it is important to obtain a product with a low content of detrimental metals and especially with a low copper content. It is therefore highly desirable to reduce the metal content of rubber as far as possible, and this applies especially to rubber types having a high initial metal content. A high metal content may be due to several different causes, e. g. to the high metal content of the natural latex or to impurities which may have been introduced into the latex during the pretreatment. Synthetic dispersions of rubber usually contain detrimental metal compounds originating from the apparatus.

Dissolved metal compounds can be removed with the serum constituents of latex by creaming, centrifugal action or other known operations. Any metal compounds occurring in the latex in the form of flocs which tend to settle by gravity can be removed by clarification.

The present invention relates to a process whereby the metal compounds, especially the copper compounds, present in the latex, on or in the rubber particles in undissolved condition, are converted into soluble compounds and then removed by methods known per se for the removal of soluble compounds from rubber dispersions. According to the invention the solubilization of the metal compounds is accomplished by converting the metals into soluble complex metal compounds and removing these solubilized compounds, e. g. by dialysis, creaming, centrifugal action, adsorption or other known methods. A very suitable method for the conversion of the metal compounds present in latex into complex soluble compounds comprises the treatment of the rubber dispersion with a soluble cyanide, such as an alkali metal cyanide. Copper as well as iron and manganese compounds are solubilized according to this process.

In the absence of appreciable sulfide-ions in the liquid the copper compounds can also be

converted into other complexes. For example, tartrates, citrates, polyhydric alcohols and other soluble polyhydric organic compounds form complexes and tend to solubilize any copper present.

The solubilization of the insoluble metal compounds can, if desired, be effected while other operations are being conducted, e.g. during hydrolysis with alkali-lye or during other purification operations. The solubilization of detrimental metal compounds in the rubber dispersions must ordinarily be effected in practice in an alkaline medium in order that the dispersion may remain stable. The removal of the metal complexes from the rubber must likewise be effected in an alkaline medium and therefore before the coagulation, which is usually conducted in an acid medium.

By employing an alkali cyanide to produce complex formation and solubilization of the metal content, as described above, the copper content, for example, of the rubber can be decreased to $\frac{1}{4}$ or less of the original content. The amount of cyanide used is preferably as low as possible. It has been established by experiment that it is possible to obtain a considerable decrease of the copper content when small amounts, such as 30 mg. of cyanide per liter are used. Such an addition will result in a decrease of the copper content from an initial value of e.g. 0.86 mg. per 100 g.

to about 0.51 mg. copper per 100 g. of rubber. In practice amounts of 0.1 to 0.2 g. cyanide per liter are to be recommended. When the last mentioned amounts are added the copper content of such a rubber can be reduced to as low as 0.23 mg. of copper per 100 g. of rubber. The other metals are reduced in a corresponding manner.

Heating of the dispersion to which the cyanide has been added promotes the solution of the metals such as copper and with such heating the use of smaller amounts of cyanide is sufficient. Without heating, larger amounts of cyanide must be used in order to produce a final metal content within the range of 0.2 to 0.25 mg. of copper per 100 g. of rubber. The dispersions may be heated to temperatures somewhat below or at the boiling point, for example.

The removal of solubilized copper can be accomplished by various methods, e.g. by centrifugal action, creaming, dialysis adsorption, ultrafiltration etc. The removal by creaming with the aid of Konnyaku starch is especially suitable, since a considerable decrease of the copper content of the final rubber product is obtained thereby. Possibly the copper is adsorbed by the Konnyaku starch and the unexpected decrease of the copper content is possibly due to such an adsorption.

GODFRIED JOHAN VAN DER BIE.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF CHLORO-2-BUTADIENE, 1,3 (CHLORO- PREN)

Stanislav Landa, Zlin, Bohemia and Moravia;
vested in the Alien Property Custodian

No Drawing. Application filed August 20, 1941

The method relates to the production of chloropren from acetylene and hydrogen chloride or from vinylacetylene and hydrogen chloride at a temperature, which is higher than 110° C. According to the invention the gases to be reacted are conducted over a catalyst, which consists of a solid carrier, such as for instance kaolin, pumicestone or silicagel impregnated with cuprous- and ammonium-chloride. The employment of cuprous- and ammonium-chloride without carrier in solution to the synthesis of chloropren from vinylacetylene and hydrogen chloride is known. In a former patent of the inventor a catalyst is mentioned for the direct synthesis of chloropren, which catalyst consists of cuprous- and ammonium-chloride strewed in powderous state on active coal. For the direct synthesis of chloropren from acetylene and hydrogen chloride or for the synthesis of chloropren from vinylacetylene and hydrogen chloride there has never been used a catalyst of the above described composition. The supposition, that at higher temperature compounds with higher content of chlorine (for instance dichlorine butene) will form has proved to be incorrect.

Example 1

Shaped bodies are pressed from moist kaolin and impregnated with a solution of 200 g cuprous-chloride and 100 g ammonium-chloride in 100 g water. The shaped bodies thus impregnated are dried in a flow of hydrogen or nitrogen. Over 450 cm³ of these shaped bodies a mixture of 2 parts acetylene and 1 part hydrogen chloride is conducted at 180°-200° C at a speed of 400 cm³ per minute. In the receiver collects, within a short time, 100 cm³ of a liquid which contains more than 80% chloropren. The content in dichlorine-butene does not exceed 10%.

Example 2

From similar parts of moist kaolin and infusorial earth shaped bodies are produced, which

are impregnated with a similar solution as that indicated in example 1 and dried in a flow of hydrogen. Over 450 cm³ of these shaped bodies a mixture of 2 parts acetylene and 1 part hydrogen chloride is conducted at 180°-200° C at a speed of 400 cm³ per minute. In the receiver collects then within a short time 100 cm³ of a liquid, which at a distillation test showed 90% of chloropren.

Example 3

Over shaped bodies, which were prepared in the same manner as in the example 1 or 2, a mixture of similar parts vinylacetylene and hydrogen chloride was conducted at 180° C at a speed of 400 cm³ per minute. In the receiver chloropren, which contained approximately 10% dichlorine-butene, condensed.

Example 4

The experiment was carried out in the same manner as in the example 3, but the temperature was increased to 200° C and the speed to 500 cm³ per minute. Also in this instance almost pure chloropren was obtained.

Example 5

Pumicestone was impregnated with a solution of cuprous- and ammonium-chloride same as the shaped bodies from kaolin in example 1 and dried in a flow of hydrogen. A tube was filled with pieces which were smaller than peas and 2 parts acetylene and 1 part hydrogen-chloride were conducted through the tube at 200° C. In the receiver almost pure chloropren condensed.

A carrier is preferably employed, which itself shows no activity. By the invention the following advantages are obtained: The reaction takes place very rapidly. Corrosions are reduced to a minimum, as dry gases are employed. The catalyst has a great duration and the reaction product possesses a great purity.

STANISLAV LANDA.

ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING MIXTURES OF POLYSTYRENE WITH NATURAL OR SYNTHETIC RUBBER

Hans Müller, Berlin - Wilmersdorf, and Franz Zeplichal, Berlin - Charlottenburg, Germany; vested in the Alien Property Custodian

No Drawing. Application filed September 29, 1941

This invention relates to a method of producing mixtures of polysyrene with natural or synthetic rubber.

The mixture of polystyrene with india-rubber must be effected at a temperature lying above the softening point of polystyrene, since otherwise the polystyrene cannot be homogeneously distributed within the india-rubber. It has been found that the mixtures thus produced after cutting off the skin from the hot roller and when cooled are hard and brittle and break at room temperature.

Tests have surprisingly shown that the mixture becomes again flexible and supple and maintains these properties, if it is, for instance, subsequently subjected to a cold rolling.

According to the invention the constituents when producing mixtures of polystyrene with natural or synthetic rubber are therefore first mixed at a temperature lying above the softening point of the polystyrene and the mixture when cooled is subjected to a further deformation, particularly on cold rollers at a temperature below the softening point of polystyrene.

The invention is of particular importance for the production of synthetic rubber mixtures, in which case by synthetic rubber are to be understood particularly the artificial substances containing polymers and interpolymers of butadiene and its derivatives.

For different electro-engineering purposes, such as, for instance, for the insulation of conductors serving to transmit high-frequency alternating currents, so-called para-mixtures have hitherto been employed, i. e., india-rubber mixtures which do not have an organic loading and whose percentage of india-rubber varies approximately from 80 to 95%. Such mixtures cannot be produced with synthetic rubber, since mixtures having such a high percentage of synthetic rubber owing to their great toughness cannot be calendered and not even applied to conductors with the aid of the extrusion press.

In order that this may be possible, a considerable amount of softening agent had to be added to the synthetic rubber. However, the best softening agents as is well known are not satisfactory from a dielectric point of view. It is true that a softening of the synthetic rubber may be attained with the known softening agents; however, such mixtures cannot be calendered and extruded to obtain a completely smooth surface.

According to the invention it is possible to produce mixtures of synthetic rubber which meet all requirements both from a mechanical and dielectrical point of view.

Since the insulation of electric conductors produced from such mixtures must be vulcanized and since the temperature at which the vulcanization is effected lies above the softening point of

the normal polystyrene, the rolled or extruded mixture would thereby become again brittle. According to the invention a highly molecular polystyrene whose softening point lies above the vulcanizing temperature is employed for the production of vulcanizable mixtures of polystyrene with synthetic rubber. To this end, above all, types of polystyrene with a K-value of 100 and over are employed, such as are, for instance, obtainable under the trade name "polystyrene EF".

Such vulcanizable mixtures according to the invention which preferably contain 25 to 100 parts by weight of a highly molecular polystyrene having a softening point of about 175 degrees centigrade and 100 parts of synthetic rubber may be very easily calendered into a smooth sheet or extruded so as to apply a smooth insulation covering on conductors and are characterized by very low values of the dielectric losses and of the dielectric constant. Only the vulcanizing agents and vulcanization accelerators necessary therefor are preferably added to the mixture. Under circumstances further small amounts of softening agents adapted for insulation purposes, such as coumarone resin, liquid butadiene polymers, fatty acids, paraffin or the like may, however, be added thereto.

Another field of application for which the invention is of great importance is the production of soft rubber parts for sealing purposes and the like which should be particularly soft and elastic. To this end, rubber regenerates alone or mixed with another substance are also employed to a great extent which behave in a similar manner as synthetic rubber as regards the capability of being calendered into a smooth sheet or so extruded as to apply a smooth insulation covering on conductors. Such mixtures must often be capable of being extruded or calendered and vulcanized without the use of molds, in which case neat and smooth surfaces are necessary. While mixtures consisting of synthetic rubber or rubber regenerate do not fulfil both conditions, it is possible according to the invention to considerably improve the mixture by adding small amounts, for instance, only 1 to 5% of a polystyrene having a softening point lying above the vulcanizing temperature so that it may be easily calendered or extruded without impairing the quality of the final product.

Thus, it is possible, for instance, by adding 1% of a highly molecular polystyrene in form of a polystyrene-rubber batch to a mixture difficult to calender and containing 20% synthetic rubber and 40% rubber regenerate to improve the properties of the mixture to such an extent that it may be calendered into sheets or extruded into tubes whose surfaces are perfectly smooth.

HANS MÜLLER.
FRANZ ZEPlichal.

ALIEN PROPERTY CUSTODIAN

SYNTHESIS OF MULTI-LINK HYDROCARBONS FROM HYDROGEN AND CARBON MONOXIDE

Walter Feisst, Otto Roelen, and Walter Schuff,
Oberhausen-Holteln, Germany; vested in the
Alien Property Custodian

No Drawing. Application filed October 14, 1941

This invention relates to the Fischer-Tropsch process of synthesis of multi-link hydrocarbons from hydrogen and carbon monoxide in the presence of a suitable catalyst, and more particularly to a process of regenerating the catalyst employed in the Fischer-Tropsch synthesis.

It is an object of this invention to provide a process whereby to regenerate the catalyst which has been employed in the Fischer-Tropsch process and the activity of which has been exhausted after extended use in such process, in a more lasting and more facile manner than was heretofore possible.

Other objects and the manner in which the same are attained, will appear from the following description.

As is well known, the Fischer-Tropsch process of synthesis of multi-link hydrocarbons from hydrogen and carbon monoxide, requires the presence of a catalyst, this catalytic material relying for its catalytic activity on the presence of iron, nickel or cobalt or mixtures of these metals. Apart from these metals, the catalyst usually contains activating additions of alkalis, alkaline earth, magnesium, rare earth, thorium, copper or manganese. The catalytically active metals and their activating additions may be precipitated on carrier substances such as kieselguhr or the like.

When such catalyst has been used in the Fischer-Tropsch process over a certain length of time, its efficiency begins to drop. This reduction in activity is mainly due to the fact that high-molecular organic substances produced in the process are deposited on the catalyst. Over a certain period, the catalytic activity of such catalysts may be restored by methods of treatment whereby the high-molecular organic deposits are removed from the catalyst. Thus, for example, the weakened catalyst may be treated at synthesis temperature with hydrogen or a suitable liquid. While such measures for the regeneration of the catalyst may be frequently repeated, it has been found that in the end the high-molecular organic substances adhere so tenaciously to the catalysts that more drastic measures are to be employed, these measures including dissolution of the contact substance and subsequent restoration by re-precipitation of the catalytic metals. This procedure, however, was found to be accompanied by the disadvantage that the deposits remaining in the contact substance materially increase the difficulty of restoring the catalyst. Thus, for example, the filtration of the metal salt solution produced by decomposition with acid is rendered

more difficult by the presence of high-molecular paraffins contained in the spent catalyst. Moreover, the re-precipitation of the catalytic metals is affected by the fatty acids and other oxygen containing compounds which are produced from the paraffins on the dissolution of the catalysts in nitric acid, the compounds referred to preventing precipitation by the formation of complexes. In view of these drawbacks, the prior art lacked any satisfactory method of completely regenerating the catalyst once the treatments at synthesis temperature of the partly weakened catalyst were no longer of any avail.

According to the present invention, the aforementioned drawbacks are eliminated, and a very satisfactory procedure of regenerating the completely spent catalyst is arrived at in the following manner. Prior to the dissolution in acid, the spent catalyst is subjected to a preliminary treatment wherein hydrogen is passed over the spent catalyst at a temperature materially in excess of the synthesis temperature. While the main requirement is that the temperature of the preliminary treatment should be materially in excess of the synthesis temperature, a temperature above 300°C is generally indicated. Preferably this temperature should even exceed 350°C, a preferred range for the temperatures useful in carrying out this preliminary treatment with hydrogen being between about 350°C and about 400°C. We have found that this preliminary treatment completely removes the organic substances from the catalysts, and it is by virtue of this complete removal of the objectionable deposit that after the preliminary treatment has come to an end the catalytic material may be dissolved in an acid and the catalytically active metals may be re-precipitated without the occurrence of any such detrimental effects as were enumerated above.

In the preliminary treatment with hydrogen, if it is desired to recover by itself the high-melting hard paraffin that may be separated from the spent catalysts, it is advisable to extract the catalysts with a suitable solvent or a suitable scouring agent prior to carrying out the preliminary treatment with hydrogen. Preferably this extraction step should proceed at temperatures which exceed the melting points of the hard paraffins. This extraction of the spent catalysts not only results in the recovery of the high-melting point paraffin, but moreover has the added advantage that when the extraction is followed immediately by the preliminary treatment with hydrogen, there results a substantial saving of this gas.

The time required for removing the organic deposits from the catalysts depends upon the temperatures employed and the velocity at which hydrogen is passed over the catalytic material. Increases of this velocity and increases of these temperatures tend to shorten the time period required for the preliminary treatment of the catalysts. Thus it was found that the deposited organic substances could be completely removed from the contact substance within half an hour by passing the hydrogen thereover at temperatures from 350° to 400°C and at a velocity of from 50 to 60 l per hour per sq. cm. This time period, however, may be further reduced by additional increases in the velocity and the temperature of the treatment.

If it is desired to eliminate the pyrophoric properties of the contact substance so that it may be brought into contact with the atmosphere without any danger of spontaneous combustion, a certain amount of steam may be added to the hydrogen employed in the preliminary treatment of the contact substance, or else the preliminary treatment with hydrogen may be followed by a subsequent treatment with steam, the oxidizing action of the steam removing in both instances the pyrophoric properties of the contact substance.

Example

A cobalt catalyst of the type conventionally employed in the Fischer-Tropsch process of synthesis of multi-link hydrocarbons from hydrogen and carbon monoxide, which had been reactivated a great many times in the synthesis furnace by treatment with hydrogen at synthesis temperature until its activity had finally totally departed, is treated with a rapidly flowing stream of hydrogen at 350°C. After the lapse of two hours the catalytic mass has lost about 40% of its weight, paraffin and other organic substances having been withdrawn from the catalyst with the hydrogen, 80 to 85% of organic substances removed from the catalyst in the form of a paraffin with a melting point of from 60 to 65°C being obtained. The catalytic mass which under the hydrogen treatment has lost practically all organic substances previously deposited thereon, after cooling, is moistened with water and dissolved in nitric acid. The catalytically active metals are precipitated by means of a soda solution from the metal salt solution thus obtained, after purification by filtration. The washed and dried catalyst is then reduced with hydrogen and now is again available for use in a Fischer-Tropsch synthesis.

WALTER FEISST.
OTTO ROELEN.
WALTER SCHUFF.

ALIEN PROPERTY CUSTODIAN

SOLID ADDITION COMPOUNDS

Johann Rosický, Moderschan, near Prag, Bohemia
and Moravia; vested in the Alien Property Custodian

No Drawing. Application filed October 14, 1941

My invention relates to compounds solid at room temperature deriving from pyridine derivatives and more particularly from pyridine- β -carboxylic acid diethyl amide. The invention also includes methods for producing solid compounds of this kind.

The diethyl amide of the pyridine- β -carboxylic acid is known in the medicine as a stimulant for the circulation of the blood and for the respiration. In liquid state it is delivered in the form of its aqueous solutions. This manner is often disadvantageous, more particularly in cases where the amide shall be combined with solid or insoluble substances.

It has now been found that the pyridine- β -carboxylic acid diethyl amide is capable of forming with sulfanilic amide and its isomeres, called metanilic acid, labile addition compounds which are solid and in part crystalline and which can easily be worked up to tablets. The linkage is loose and the addition compounds, when dissolved in or recrystallized from water, dissociate easily into the components. From solvents free of water however they can be recrystallized with ease and recovered as beautifully formed crystals.

The new compounds may be obtained by mixing pyridine- β -carboxylic acid diethyl amide with sulfanilic amide and/or its isomeres in molecular proportions or with an excess of one of the components, if desired with heating, preferably above the melting point of the addition compound, or with the aid of a solvent.

The new compounds thus obtainable are therapeutically valuable substances which are determined as to their qualities by the properties of the components contained therein. Moreover, the combination as such results in further advantages for certain indications and mainly for the treatment of bacterial infectious diseases.

It is known that sulfanilic amide and its isomeres reduce the respiration of the cells and tissues and by this property bring about toxic secondary phenomena. In addition thereto the sulfanilic amide and its isomeres by their action on the central nervous system cause, if applied in larger doses, paralysis reactions of the nervous system.

I have now observed that centrally acting stimulants can to a great extent abolish the appearance of the nervous symptoms in an acute poisoning with sulfanilic amide in experiments on

animals. The stimulating action on the circulation and the respiration of the new compounds manifests itself in a reduction of the toxicity of the sulfanilic amide by an increase of the oxidizing processes in the organism.

It is further known that in the treatment of infectious diseases the maintenance of intensive actions of the circulation and respiration organs is of outmost importance. The diethyl amide of the pyridine- β -carboxylic acid is to a great extent used for this purpose.

It will be seen from these explanations, that not only a technical advantage is achieved with the new compounds, viz. the conversion of the liquid diethyl amide of pyridine- β -carboxylic acid into a solid substance ready for tableting, but that the new compounds are moreover distinguished by an appropriate combined effect. The stimulating action on the oxidizing processes and the thereby increased resistancy of the organism against the infection is supplemented by the specific chemico-therapeutic action of the sulfanilic amide component. In comparison with separate delivery of pyridine- β -carboxylic acid diethylamide and a sulfanilic amide derivative the use of the new substances according to this invention secures the advantages that these compounds can uniformly be applied and precisely dosed and are in the handy form of tablets.

Example 1.—172 grams finely powdered sulfanilic amide are added with stirring to 178 grams pyridine- β -carboxylic acid diethyl amide. Heat is spontaneously developed. The mixture is thereupon for a short time heated to 180° C. After cooling the reaction mixture solidifies and forms a finely crystallized substance with a melting point of 92° C. If dissolved in, or recrystallized from, water this substance decomposes into its constituents.

Example 2.—178 grams pyridine- β -carboxylic acid diethyl amide and 172 grams sulfanilic amide are commonly heated with 1500 ccms methyl acetate until dissolved. After cooling down the addition compound crystallizes in compact crystals showing a melting point of 92–93° C.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

JOHANN ROSICKÝ.

ALIEN PROPERTY CUSTODIAN

PRODUCING SULFUROUS ORGANIC COMPOUNDS

Bruno Böttcher, Kronach, Bavaria, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed October 14, 1941

The present invention relates to a method of producing sulfurous organic compounds and consists in treating with elementary sulfur at temperatures above 175° C hydrocarbons the derivatives and substitutes respectively of which contain at least one $\text{CH}=\text{C}<$ group.

It is well known that by the action of sulfur upon unsaturated organic compounds more or less instable sulfur addition products are obtained. This method was carried out by heating to temperatures between 150° and 170° C for a longer period of time linaloe oil, linalyl acetate or lavender oil. Moreover, it is known that instead of these alcohols or esters of the terpene row, pure terpenes, free of oxygen also were subjected to the action of sulfur at temperatures up to 150° C, whereby also sulfur addition products were obtained.

Furthermore, from the technics it is known that by the treatment of terpenes or their derivatives with elementary sulfur, so-called balsams are produced which technically are employed for the production of ceramic precious metal colors. It is also known that by the action of sulfur upon unsaturated organic compounds under known conditions derivatives of thiophenes of the most various constitution may result.

Now, the new mode of operation consists in heating to temperatures above 175° C certain initial substances, i. e. organic compounds containing at least one $\text{CH}=\text{C}<$ group, with elementary sulfur or compounds easily delivering sulfur, for instance sulfur chloride or poly sulfides. It has been found that the observations made by earlier investigators that the addition of sulfur to unsaturated compounds at temperatures below 175° C was effected rather slowly on the one hand and on the other hand led to not well defined compounds. More or less oil-like substances with various sulfur content only were obtained.

However, if heating is effected to temperatures above 175° C, the sulfur is added to the double bond in a stoichiometrical proportion. Consequently the method according to the invention consists in producing sulfurous organic compounds from hydrocarbons the derivatives and substitutes of which contain at least one $\text{CH}=\text{C}<$ group by treating these compounds with elementary sulfur in which the proportion of sulfur to non-sulfurized initial substance corresponds about to the proportion of 3 atoms of sulfur to one vinyl group each in the initial substance and heating the initial substances together with said sulfur to temperatures of above 175° C.

Examples

1. Anetholl with sulfur in a proportion of 1 mol:3 atoms is heated in an open container to temperatures between 190° to 230° C. At this

temperature a prominent reaction is effected. After cooling the mass, a substance re-crystallizable from organic solvents, as alcohol or acetone, remains.

This sulfurous substance supplies easily crystallizable metal compounds and also additional products, as for instance products saturated or unsaturated with halogen alkyls the halogens of which in turn may be exchanged, for instance by hydroxyl groups. These well defined sulfurous compounds have disinfecting properties and are otherwise also valuable from a therapeutic stand of view.

2. Myrcene or an ethereal or volatile oil containing mircene, for instance bay oil, is heated with sulfur in the same mol proportion as described above to a temperature of 200° to 210° C. Above 200° C a prominent reaction results during which the mass strongly swells then drops back again and finally during cooling leaves a caoutchouc-like mass.

The constitution of the newly formed body is not known. It may, however, be supposed that here a polymerisation with simultaneous addition of sulfur comes into consideration in which the sulfur probably has entered into the $\text{CH}=\text{C}<$ group, whereas the $\text{C}=\text{CH}_2-$ groups at the end of the carbon chain have rendered possible the polymerisation.

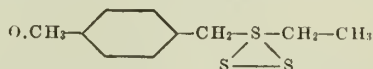
The above example shows that sulfurous products of polymerisation having caoutchouc-like properties may be obtained from unsaturated organic compounds which contain $\text{C}=\text{CH}_2-$ groups at the end of the carbon chain as well as a $\text{CH}=\text{C}<$ group in the molecule.

This reaction is not limited to bodies having the constitution stated in the preceding examples. The supposition only is of importance that always at least one $\text{CH}=\text{C}<$ group is present in the molecule and the entrance of the sulfur is effected at temperatures of above 175° C.

So, for instance, if anethole of the constitution



is treated in accordance with the present invention with sulfur, a substance is obtained having 3 atoms of sulfur in the molecule and which may be represented by the formula



and for which the ring of the 3 sulfur atoms is characteristic.

The same result is obtained if corresponding other initial substances are used which always must correspond to the requirements stated regarding the above mentioned double bonds.

BRUNO BÖTTCHER.

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF ADDITION PRODUCTS FROM DIENES AND COMPOUNDS HAVING AN UNSATURATED CARBON LINKAGE ACTIVATED BY SUBSTITUENTS

Heinrich Hopff and Curt W. Rautenstrauch, Ludwigshafen-on-Rhine, Germany; vested in the Alien Property Custodian

No Drawing. Application filed October 17, 1941

The present application has been divided out from our copending application Serial No. 274,040, filed May 16, 1939.

The present invention relates to an improved process of producing addition products.

It is already known that dienes will add on to compounds having a double or triple carbon linkage, which are activated by substituents, with the formation of cyclic compounds. This reaction is usually carried out by heating about equimolecular amounts of the initial materials, if desired in the presence of organic diluents, and proceeds generally speaking very vigorously. By reason of the turbulent course of the reaction, side-reactions readily occur which lead to a reduction in the yield or contamination of the reaction products.

We have now found that addition products of dienes and unsaturated compounds having a double or triple carbon linkage activated by substituents are obtained in a smooth and non-objectionable manner by carrying out the reaction in aqueous dispersion in the absence of substances favoring polymerization, advantageously even in the presence of agents preventing polymerization. It is preferable to produce the dispersion by the addition of dispersing or emulsifying agents which promote the solubility of the reaction components in water. Among dienes, i. e. compounds having reactive conjugated double carbon linkages, there may be mentioned butadiene and its substitution products, as for example isoprene, dimethylbutadiene and beta-chlorbutadiene, and also cyclopentadiene, cyclohexadiene, pyrrole and furane. Among substances having a double or triple carbon linkage which is activated by substituents, there may be mentioned especially those having substituents containing a double or triple bond in alpha-position to the said double or triple carbon linkage, as for example of maleic anhydride, maleic esters, as for example maleic acid diethyl or dibutyl esters, maleic acid imides, as for example maleic acid methyl imide or isobutyl imide, and the corresponding derivatives of substituted maleic acids, as for example chlormaleic acid, vinyl compounds having a carbonyl group adjacent to the vinyl group, such as acrolein, vinyl methyl ketone, and also crotonaldehyde, cinnamic aldehyde, cinnamic acid esters, acrylic acid and its homologues and derivatives of the same, as for example acrylic and methacrylic esters, and also quinones, such as benzoquinone, naphthaquinone and chloroquinones, and also vinylpyridine, vinyl-furane, nitroalkenes, such as nitropropene,

omega-nitrostyrene, acetylene dicarboxylic acid esters, monovinyl or divinyl acetylenes, and also butadienes and further vinyl esters, vinyl chloride, vinyl ethers, N-vinyl compounds, as for example N-vinylcarbazole and N-vinylpyrrole. Substituents which effect an activation of the double or triple carbon linkages are quite generally positive or negative substituents as may be seen from the foregoing.

Suitable dispersing or emulsifying agents, of which even comparatively small amounts are sufficient, are for example alkylated naphthalene sulphonic acids, sulphuric esters of higher fatty alcohols, addition products of several molecules of ethylene oxide to long-chain organic compounds containing hydroxyl or amino groups, and also the taurides of higher fatty acids or sulphonated fatty acid amides.

In many cases small additions of alcohols, as for example normal butyl alcohol, or of highly polymerized organic compounds having dispersing action, as for example polyvinyl alcohol, polyacrylic acid sodium salt and watersoluble cellulose derivatives are suitable as dispersing agents.

Among agents preventing polymerization there are suitable for example substances of phenolic character, amines, inorganic and organic sulphur compounds and frequently also metallic copper or copper salts.

The reaction usually takes place at relatively low temperatures, as for example between 10° and 100° C. It is sometimes preferable to add buffer substances, as for example inorganic or organic acids or bases and sometimes also salts, such as sodium acetate, potassium bisulphate or primary sodium phosphate.

Usually quantitative yields of the reaction products in a state of excellent purity are obtained. By reason of the effective withdrawal of heat of reaction by the water present, no undesirable increases in temperature take place and therefore no injurious side reactions. Moreover the reaction may be carried out at a speed sufficient in practice even with difficultly reacting substances under mild conditions.

The following Examples will further illustrate how this invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight.

Example 1

74 parts of N-isobutyl maleic imide are suspended in 150 parts of water to which 4.5 parts of an amine oxide obtained by treatment of dimethyldodecylamine with hydrogen peroxide

have been added, and 44 parts of butadiene are added. The whole is shaken at room temperature in a pressure-tight vessel. After 12 hours, the whole is poured into a solution of 0.5 part of aluminium sulphate in 150 parts of water, crystals of the N-isobutyl-tetrahydro-phthalimide formed thus soon separating in practically a quantitative yield. The compound boils at from 148° to 150° C at a pressure of 12 millimeters (mercury gauge) and passes over as a colorless oil which soon solidifies to white crystals which melt at 40° C.

Example 2

162.5 parts of N-isobutyl maleic imide are suspended in 500 parts of water to which 10 parts of an addition product of 40 molecules of ethylene oxide to 1 molecule of castor oil have been added. 87.5 parts of dimethylbutadiene are added and the whole stirred vigorously at 40° C. After 12 hours the whole is allowed to cool and the precipitated colorless crystals are filtered off by suction. The yield is quantitative. The N-isobutyl-dimethyl-tetrahydro-phthalimide formed melts at 73° C.

Example 3

75 parts of cyclopentadiene are added to a dispersion of 175 parts of isobutyl maleic imide in 500 parts of water to which 10 parts of the addition product of 20 molecules of ethylene oxide to 1 molecule of dodecyl alcohol have been added. The whole is stirred vigorously at 25° C. After 6 hours, the precipitated crystals of the N-isobutyl-ene-dimethyl-tetrahydrophthalimide formed are filtered off by suction. The compound smells like camphor, is colorless and melts at 73° C. The yield is practically quantitative.

Example 4

114 parts of dimethylbutadiene are emulsified in 500 parts of water to which 10 parts of the emulsifier specified in Example 2 and 5 parts of sodium acetate have been added. 136 parts of maleic anhydride are then added rapidly and the whole stirred at 40° C. After 12 hours, the deposited crystals are filtered off by suction. Dimethyl-tetrahydrophthalic acid is obtained in a good yield.

Example 5

150 parts of dimethylbutadiene are emulsified in 500 parts of water to which 5 parts of the emulsifier specified in Example 2 and 5 parts of sodium acetate have been added. 100 parts of acrylic nitrile are then added and the whole stirred vigorously at 50° C. After 12 hours the resulting emulsion is poured into a solution of 5 parts of aluminum sulphate in 500 parts of water and, after cooling, the organic layer is separated. Dimethyl-tetrahydro-benzonitrile having a boiling point of 96° C at a pressure of 12 millimeters (mercury gauge) is thus obtained in a good yield.

Example 6

142 parts of benzoquinone are suspended in 500 parts of water containing 10 parts of the emulsifier specified in Example 3 and 5 parts of sodium acetate. 108 parts of dimethyl-butadiene are then added and the whole is stirred at 40° C. After 12 hours, the whole is cooled and the deposited pale yellow crystals of the resulting dimethyl-hexahydro-naphthoquinone having a melting point of 117° C are filtered off by suction. The yield is quantitative.

Example 7

172 parts of maleic acid diethyl ester are emulsified in a solution of 5 parts of the emulsifier specified in Example 2 and 5 parts of sodium acetate in 500 parts of water and 82 parts of dimethylbutadiene are added. The emulsion is stirred at 60° C for 24 hours and, after cooling, poured into a solution of 10 parts of aluminum sulphate in 500 parts of water. The organic layer is separated and distilled. The boiling point of the resulting tetrahydro-phthalic acid diethyl ester is from 129° to 130° C at a pressure of 1 millimeter (mercury gauge).

Example 8

53 parts of acrylic nitrile are emulsified in 150 parts of water containing 4.5 parts of the emulsifier specified in Example 1 and 5 parts of sodium acetate. 50 parts of butadiene are then added and the resulting emulsion is shaken for 24 hours in a pressure-tight vessel at room temperature and then poured into a solution of 5 parts of aluminum sulphate in 200 parts of water. The organic layer is separated and distilled. The boiling point of the resulting tetrahydrobenzonitrile is 188° C.

Example 9

74 parts of isoprene are emulsified in a solution of 10 parts of the emulsifier specified in Example 3 and 1 part of hydroquinone in 500 parts of water, 166 parts of N-isobutylmaleic imide are added and the whole stirred for 24 hours at 40° C. Sodium sulphate is then added and the organic layer formed is separated and distilled. Methyl-tetrahydro-N-isobutyl-phthalimide having a boiling point of from 156° to 157° C at a pressure of 11 millimeters (mercury gauge) is thus obtained.

Example 10

960 parts of benzoquinone are suspended in an emulsion of 480 parts of butadiene in 6000 parts of water containing 25 parts of the emulsifier specified in Example 3. After stirring for 12 hours in a pressure-tight vessel at 50° C, the whole is cooled. The deposited crystals of tetrahydronaphthoquinone having a melting point of 54° C are separated. This changes, even by drying at 80° C, rapidly into the isomeric dihydronaphthohydroquinone having a melting point of 207° C. The yield is 80 per cent of that theoretically possible.

Example 11

4000 parts of maleic acid isobutyl ester are emulsified in an emulsion of 1000 parts of butadiene in 10,000 parts of water containing 100 parts of the emulsifier specified in Example 2, 10 parts of hydroquinone and 100 parts of sodium acetate, and stirred at 70° C in a pressure-tight vessel. After 24 hours, common salt is added and the separated organic layer distilled. The tetrahydro-phthalic acid isobutyl ester thus obtained boils at from 126° to 127° C at a pressure of 0.5 millimeter (mercury gauge).

Example 12

120 parts of maleic acid isobutyl imide are emulsified in a solution of 10 parts of the emulsifier specified in Example 1 and 5 parts of sodium acetate in 500 parts of water at 50° C. 50 parts of pyrrole are added and the whole stirred for 6 hours at 50° C. After cooling, sodium sulphate solution is stirred in and the organic layer is

separated; it soon solidifies to a crystal cake. Tetrahydroendo-N-phthalimide is thus obtained which melts at 122° C after recrystallization from methanol.

Example 13

137.5 parts of benzoquinone are suspended in an emulsion of 112.5 parts of 2-chlorbutadiene in 500 parts of water containing 10 parts of the emulsifier specified in Example 2. After stirring for 12 hours at 40° C, the whole is cooled to 4° C and the precipitate formed is filtered off by suction. The tetrahydro-beta-chlornaphthoquinone formed in a yield of 95 per cent is extraordinarily sensitive to light and melts at 95° C.

Example 14

142 parts of monochlorbenzoquinone are suspended in an emulsion of 88 parts of 2-chlorbutadiene in 500 parts of water containing 10 parts of the emulsifier specified in Example 2. After stirring for 12 hours at 40° C, the whole is cooled to 4° C. The 2.7-dichlortetrahydronaphthoquinone having a melting point of 115° C thus formed is thus precipitated.

Example 15

460 parts of butadiene are emulsified in a pressure-tight vessel in 2200 parts of an aqueous solution of 600 parts of maleic acid, 20 parts of the watersoluble condensation product of 1 molecular proportion of octodecyl alcohol with 40 molecular proportions of ethylene oxide, 2 parts of hydroquinone and 4 parts of sodium acetate. The whole is then heated at from 50 to 60° C for 10 hours while stirring. On cooling, the tetrahydrophthalic acid formed with a good yield separates out in the form of crystals.

Example 16

114 parts of dimethyl butadiene are emulsified in 535 parts of a 34 per cent aqueous solution of maleic acid after the addition of 10 parts of the condensation product of 1 molecular proportion of castor oil with 40 molecular proportions of ethylene oxide, 5 parts of sodium acetate and 2 parts of hydroquinone. When warming the emulsion thus obtained at 40° C for 12 hours, dimethyl tetrahydrophthalic acid is formed with a practically quantitative yield.

Example 17

123 parts of dimethyl butadiene are emulsified

in a solution of 171 parts of acetylene dicarboxylic acid in 400 parts of water and added with 10 parts of the emulsifying agent specified in Example 2, 5 parts of sodium acetate and 2 parts of hydroquinone. The emulsion thus obtained is warmed at 40° C for about 30 hours. Crystals of the dimethyldihydrophthalic acid formed separate out. They are filtered off by suction and recrystallized from water, if desired. They melt at from 170 to 171° C.

Example 18

427 parts of vinyl methyl ketone and 315 parts of butadiene are emulsified in a solution containing 1600 parts of water, 40 parts of the emulsifying agent specified in Example 3, 20 parts of sodium acetate and 10 parts of hydroquinone. The whole is warmed at 60° C for 24 hours in a pressure-tight vessel while stirring. The cyclohexenyl methyl ketone formed with nearly quantitative yield is then distilled off with water vapors, separated from the water and dried by means of calcinated sodium sulphate. It boils at 78° C under a pressure of 17 millimeters (mercury gauge).

Example 19

50 parts of cinnamic aldehyde and 30 parts of dimethyl butadiene are emulsified in 75 parts of a 2 per cent aqueous solution of the emulsifying agent specified in Example 16. After the addition of 1 part of calcium carbonate the whole is heated at 90° C while stirring. After about 12 hours common salt is added. The reaction product separates out thereby readily. It boils at 125° C under a pressure of 0.6 millimeter (mercury gauge).

Example 20

70 parts of croton aldehyde and 54 parts of butadiene are emulsified in a pressure-tight vessel in 100 parts of a 2 per cent aqueous solution of the emulsifying agent specified in Example 15. After adding 1 part of calcium carbonate the whole is heated at 90° C for 24 hours while stirring. The addition product formed separates after the addition of sodium sulphate. It boils at from 58 to 60° C under a pressure of 12 millimeters (mercury gauge).

HEINRICH HOPFF.

CURT W. RAUTENSTRAUCH.

ALIEN PROPERTY CUSTODIAN

DERIVATIVES OF 1-OXYPHENYL-3-AMINO-BUTANE AND PROCESSES FOR THEIR PRODUCTION

Fritz Kulz, Frankfurt am Main, Germany; vested in the Alien Property Custodian

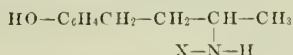
No Drawing. Application filed October 18, 1941

The invention concerns new derivatives of 1-oxyphenyl-3-aminobutane and processes for their production.

It is known that β -(p-oxyphenyl)-isopropylamine and its derivatives are characterized by a special effect on circulation.

Mannich has prepared the next higher homologue amine, the 1-oxyphenyl-3-aminobutane, from p-oxybenzylacetone, by preparing and reducing the oxim. (Archiv für Pharmazie, vol. 265, (1927), p.23). It has been stated that this compound in comparison with the above named compound has a less distinct effect on circulation, while analgesic properties may be just detectable, but are far too weak to be suited for practical purposes.

It has been found that alike the known nor-base derivatives of 1-o-, -p- or -m-oxyphenyl-3-aminobutane of the general formula



in which X represents alkyl, alkenyl, cyclo alkyl, cyclo alkenyl, aralkyl or aralkenyl have no ability of effecting circulation, but unlike the known nor-base have excellent analgesic properties. Among the alkyl derivatives, for example among the methyl-, ethyl-, propyl-, butyl-, isobutyl-, amyl-, isoamyl-derivatives the methyl derivative has strong, the butyl derivative extraordinary efficacious analgesic properties. The other alkyl derivatives have less outspoken analgesic properties. Compounds with an alkyl with more than 6 carbon atoms are less important for practical purposes. This rule is valid, independently of the position of the OH-group, that is whether it is in the o-, p- or m-position. Also alkenyl-, for example allyl-, cyclo alkyl-, for example cyclopentyl- or cyclo hexyl, cyclo alkenyl, for example cyclopentenyl or cyclo hexenyl, aralkyl-, for example benzyl-, phenyl ethyl-, or aralkenyl-, for example phenyl allyl-derivatives, have good analgesic properties.

The new analgesics may be prepared according to various methods. 1-oxyphenyl-3-aminobutane may be treated in known manner with agents, which are suited for introduction of the desired hydrocarbon rest, for example with halogenides of the corresponding hydrocarbons, or with corresponding aldehydes or ketones, in which latter case the forming Schiff's base must be hydrogenated, or according to Leuckart-Wallach.

One may, however, proceed vice versa, that is

from 1-oxyphenyl-3-halogenbutane, and react this with a primary amine.

The new compounds may also be obtained by starting from oxybenzyl-acetone, condensing same with a primary amine or ammonia and hydrogenating the forming condensation products. If ammonia is used, the obtained 1-oxyphenyl-3-aminobutane must be treated with agents, which are suitable for introduction of the hydrocarbon rest.

The most simple method of producing the compounds according to the invention consists in condensing oxybenzalacetone with primary amines or ammonia. Also in this case condensation products are obtained, the carbon carbon double bond and the carbon nitrogen double bond of which may be hydrogenated in a single working process, for example catalytically by hydrogen in the presence of platinum. If ammonia is employed for the production of the condensation products the forming 1-oxyphenyl-3-aminobutane must be treated again with agents, which are suitable for introduction of the desired hydrocarbon rest.

The compounds according to the invention may also be prepared from 1-phenyl-3-aminobutanes substituted accordingly at the nitrogen by alkyl, alkenyl, cyclo alkyl, cyclo alkenyl, aralkyl or aralkenyl by nitration in the benzene ring, reduction of the obtained nitro compound to the amino compound, diazotizing of the amino group at the benzene ring with nitrous acid and converting into the desired hydrox-y compounds by boiling.

Finally the analgesics according to the invention may be prepared from the corresponding alkoxy compounds by splitting off the etherified oxy group, for example by treatment with hydrohalogenic acid, especially hydrobromic acid. Furtheron they are obtained by saponification of the compounds acylated at the oxygen and/or the nitrogen.

EXAMPLES

(1) Preparation of 1-(p-oxyphenyl)-3-allylamino-butane

2.0 grs. of allyl bromide are added to a hot benzene solution of 5.0 grs. of 1-(p-oxyphenyl)-3-amino-butane, prepared according to Mannich and Merz, Arch. Pharm., vol. 265, p. 15 (1927). The mixture is boiled for two hours under reflux. The crystallized hydrobromide of the starting amine is filtered with suction. The mother liquor is concentrated, if necessary filtrated again from a small quantity of non-converted starting

base and evaporated to dryness. The 1-(p-oxyphenyl)-3-allylaminobutane, which is obtained in almost quantitative yield, is converted with ethereal hydrobromic acid into the hydrobromide, which, after re-crystallization from acetone, melts at 116–118° C. (uncorrected).

(2) *Preparation of 1-(p-oxyphenyl)-3-cyclopentyl-aminobutane*

5.0 grs. of 1-(p-oxyphenyl)-3-aminobutane and 2.8 grs. of cyclopentanone in methanol with 0.3 grs. of platinum oxide are shaken in an atmosphere of hydrogen. An amount of hydrogen calculated for 1 mol. substance being taken up in the course of about 2 hours, the substance is filtered from the catalyst. The methanol is evaporated and the residue taken up in ether. The 1-(p-oxyphenyl)-3-cyclopentylaminobutane is precipitated with ethereal hydrobromic acid. It melts after re-crystallization from acetone at 173 to 174° C.

(3) *Preparation of 1-(p-oxyphenyl)-3-allylaminobutane*

1-(p-oxyphenyl)-3-brom-butane is prepared by heating a mixture of 5.0 grs. of 1-(p-oxyphenyl)-3-oxy-butane, obtained according to Mannich and Merz, Arch. Pharm., vol. 265, p. 22 (1927) and hydrogen bromide in glacial acetic acid for 3 hours to 100° C. After the glacial acetic acid has been distilled off in vacuo the obtained substance is purified by taking up in ether, shaking of the ethereal solution with a solution of bicarbonate, drying and evaporation of the ether. This starting material is heated to 120–130° C. with allyl amine in great excess in a bomb tube for five hours. The excess allyl amine is evaporated. The residue is taken up in diluted hydrochloric acid, and, in order to remove neutral bodies, extracted with ether. The acid solution is rendered alkaline by help of bicarbonate. The obtained base is taken up in ether. The ether is evaporated. The residue, after having been distilled in high vacuo (boiling point 145–150° C. under 0.05 mm pressure) is converted into the hydrobromide, which melts after re-crystallization from acetone at 116–118° C. Adding on hydrobromide of same constitution prepared according to example 1 there is no depression of the melting point to be observed.

(4) *Preparation of 1-(p-oxyphenyl)-3-methylamino-butane*

5.0 grs. of p-oxybenzyl-acetone are shaken with 0.95 grs. of methylamine, solved in absolute alcohol in the presence of platinum black in an atmosphere of hydrogen. An amount of hydrogen being taken up which corresponds to 1 mol. substance the substance is worked up according to example 2. The hydrobromide of the 1-(p-oxyphenyl)-3-methylamino-butane melts after re-crystallization from water at 143° C.

(5) *Preparation of 1-(p-oxyphenyl)-3-n-butylamino-butane*

5.0 grs. of p-oxybenzylacetone and 2.3 grs. of n-butylamine solved in absolute alcohol are hydrogenated and worked up according to example 4. The residue, after evaporation of the alcohol, is heated for some time in the water-bath under vacuo, in order to remove some remaining butylamine. The hydrobromide of the 1-(p-oxyphenyl)-3-n-butylamino-butane melts after re-crystallization from water at 170° C.

(6) *Preparation of 1-(p-oxyphenyl)-3-benzylamino-butane*

5.0 grs. of p-oxybenzylacetone are hydrogenated with a solution of 3.3 grs. of benzylamine in absolute alcohol according to example 4 and are worked up according to example 5. The hydrobromide of the 1-(p-oxyphenyl)-3-benzylaminobutane melts after re-crystallization from water at 158° C.

(7) *Preparation of 1-(o-oxyphenyl)-3-n-butylamino-butane*

8.1 grs. of o-oxybenzal-acetone are treated with a solution of 3.7 grs. of n-butylamine. The red solution is shaken with platinum black in an atmosphere of hydrogen. 2 moles of hydrogen being taken up hydrogenation comes to a standstill. The solution, now practically colorless, is filtered from the catalyst, acidified with diluted hydrochloric acid and evaporated to dryness. The residue is crystallized from acetone after a small quantity of methanol is added. The hydrochloride of the 1-(o-oxyphenyl)-3-n-butylaminobutane melts at 161° C.

(8) *Preparation of 1-(o-oxyphenyl)-3-n-propylamino-butane*

3.1 grs. of o-oxybenzal-acetone are treated with 3.0 grs. of n-propylamine and worked up as described in example 7. The hydrochloride of the 1-(o-oxyphenyl)-3-n-propylamino-butane melts at 143° C.

(9) *Preparation of 1-(m-oxyphenyl)-3-n-butylamino-butane*

8.1 grs. of m-oxybenzal-acetone are treated with butylamine and worked up as described in example 7, a difference only consisting in not using diluted hydrochloric acid but diluted hydrobromic acid for acidification. The hydrobromide of the 1-(m-oxyphenyl)-3-n-butylamino-butane melts at 117° C.

(10) *Preparation of 1-(p-oxyphenyl)-3-ethylamino-butane*

8.1 grs. of p-oxybenzal-acetone are, according to example 9, converted with 2.3 grs. of ethylamine and worked up. The hydrobromide of the 1-(p-oxyphenyl)-3-ethylamino-butane melts at 130° C.

(11) *Preparation of 1-(p-oxyphenyl)-3-n-propylamino-butane*

8.1 grs. of p-oxybenzal acetone are converted with 3.0 grs. of n-propylamine and worked up according to example 9. The hydrobromide of the 1-(p-oxyphenyl)-3-n-propylamino-butane melts at 138° C.

(12) *Preparation of 1-(p-oxyphenyl)-3-n-amylamino-butane*

5.0 grs. of 1-(p-methoxyphenyl)-3-n-amylamino-butane obtained by catalytic hydrogenation of a mixture consisting of p-methoxybenzalacetone and n-amylamine in alcohol and purified by distillation (boiling point 192/194° C. at 20 mm) were heated to boiling under reflux with the ten-fold amount of constant boiling hydrobromic acid. After evaporation to dryness the residue is crystallized from water. The hydrobromide of the 1-(p-oxyphenyl)-3-n-amylaminobutane melts at 125° C.

FRITZ KULZ.

ALIEN PROPERTY CUSTODIAN

CHLORINATION OF HYDROCARBONS

Kurt R  th and Otto M  ller, Berlin-Charlottenburg, and Otto Ewald Dietzel, Castrop-Rauxel, Germany; vested in the Alien Property Custodian

Application filed October 28, 1941

The present invention relates to the chlorination of hydrocarbons in a continuous process.

It is known that on reacting chlorine and hydrocarbons mainly the respective monochlorides but at the same time also certain amounts of di- or polychlorides are formed the quantity of such higher chlorinated products increasing in proportion to the conversion of the initial hydrocarbons into monochlorides.

Wherever the maintenance of a certain lower chlorinated substitute is desired, such as monochloride alone, it has been possible to reduce the formation of higher chlorinated products to a large extent with the aid of well known modifications of the chlorination apparatus. These known modifications in the manufacture of chlorinated hydrocarbons by a continuous process, for instance in the production of monochlorides, work in such a way that the chlorine does not react directly with the total amount of the hydrocarbon to be chlorinated, but only with a divided portion of same. For this purpose the addition of chlorine is so adjusted as to yield only a small amount of monochlorides and accordingly a small amount of polychlorides. The reaction mixture is then drawn off into a still where it is separated by distillation through a fractionating column into chlorinated hydrocarbon and hydrocarbon. Whilst the chlorinated hydrocarbon gradually enriches in the still, the distilled hydrocarbon is continuously reconducted into the reaction chamber actually used for chlorination.

Fig. 1 illustrates an arrangement of apparatus according to the foregoing described principle for the manufacture of monochlorobenzene. At the outset the benzene to be treated rests in the still A whence it is distilled off over the fractionating column B into the condenser C where it is condensed and thereafter reacts with chlorine in the reaction chamber D. The chlorination gases escape through E. The chlorination product consisting of little chlorobenzene and much unchanged benzene flows continuously over an overflow back into the still A where it is separated into chlorobenzene enriching in said still, and into benzene which is reconducted into the reaction chamber over the fractionating col-

umn. It is known to effect the chlorination process in the reaction chamber D generally in the presence of a catalyst, such as FeCl₃ and under heat.

It has now been found that even under the foregoing conditions active chlorine will accompany the chlorination mixture on the return of the latter into still A where it encounters strongly enriched monochloride thus causing an unnecessarily large formation of higher chlorinated products.

According to the present invention it is possible to avoid this drawback by interposing a preferably heated sojourn zone F (Fig. 2) between the reaction chamber D and still A in which zone the active chlorine contained in the mixture returning from E is eliminated by full reaction with the hydrocarbon before reaching the still A. Said sojourn zone can have the form of an intermediate vessel, as shown in Fig. 2, but it may also be of a different suitable shape such as a coiled tube or the like. Any form of the sojourn zone is possible which leaves the reaction mixture sufficient time to eliminate the active chlorine contained therein by full reaction with the accompanying hydrocarbon.

The following quantities of active chlorine (in gram per litre) have been found in the reaction mixture flowing back into A.

Before entering the									
sojourn zone---	0,213	0,223	0,77	0,93	0,56	0,21			
After leaving the									
sojourn zone---	0	0	0	0	0	0	0		

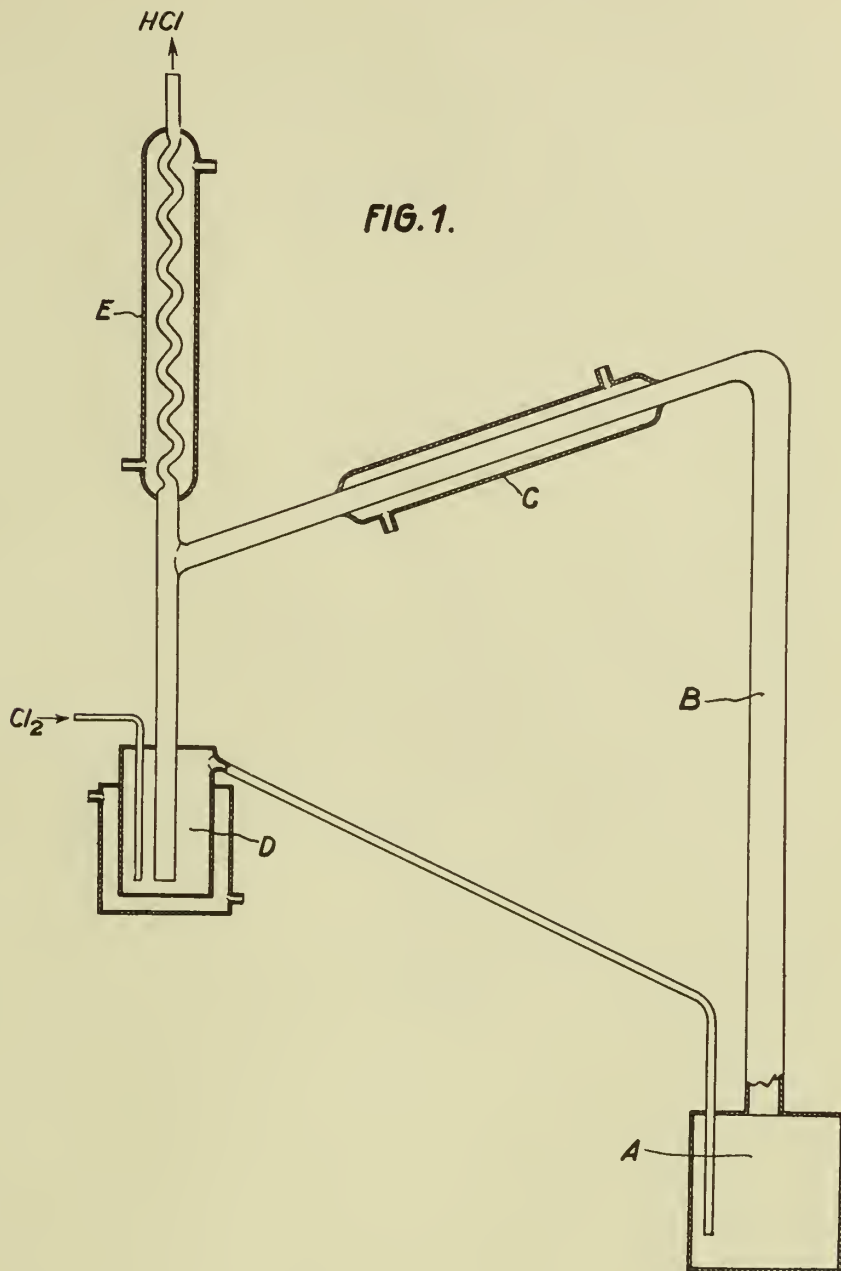
The process and apparatus described herein is used for the manufacture of monochlorobenzene, but it can also be advantageously employed both for the manufacture of any other monochlorides of hydrocarbons and for the manufacture of dichlorides or even higher chlorinated derivatives for the purpose of avoiding any further action of the active chlorine contained in the reaction mixture on the chlorinated derivative obtained.

KURT R  TH.
OTTO M  LLER.
OTTO EWALD DIETZEL.

PUBLISHED
APRIL 20, 1943.
BY A. P. C.

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CHLORINATION OF HYDROCARBONS
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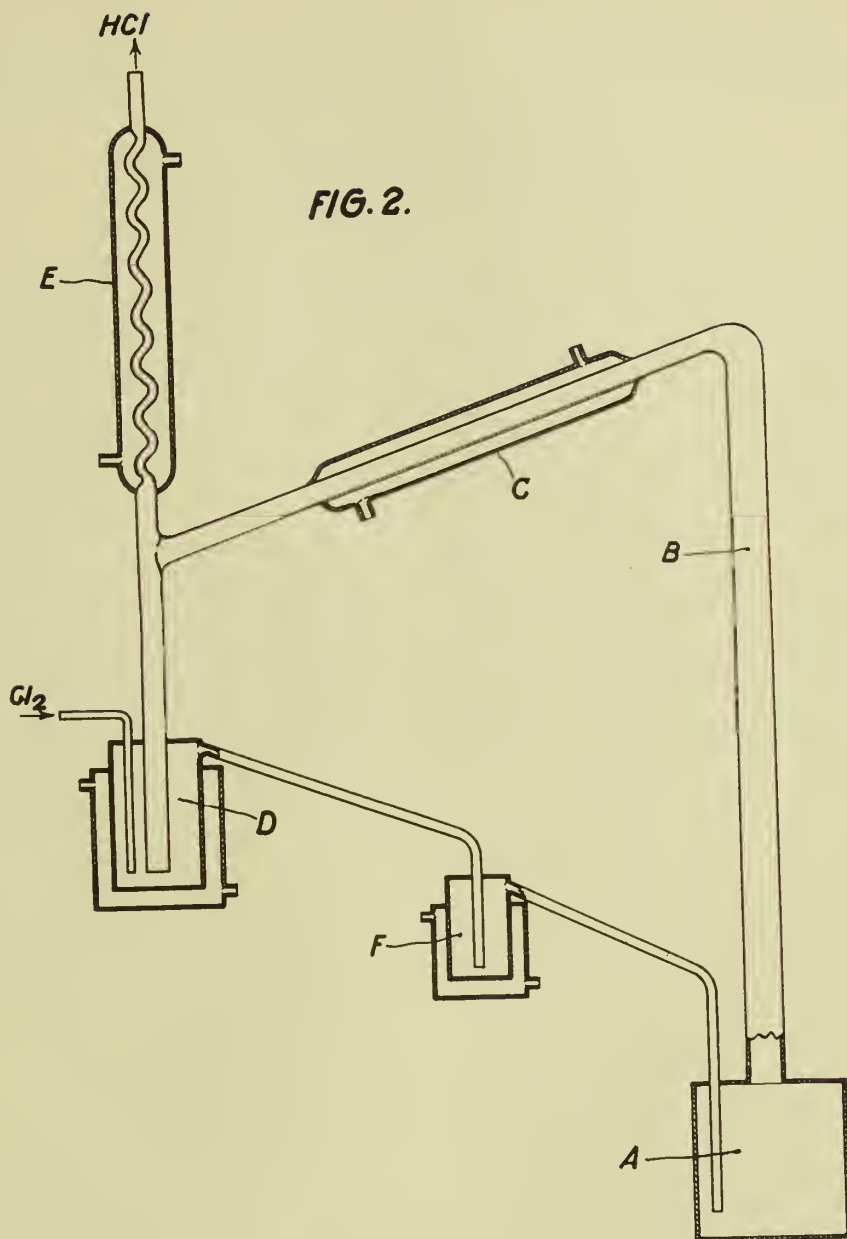


Inventors:
Kurt R  th,
Otto M  ller,
Otto Ewald Dietzsch,
by Pierce & Schoffele,
Attorneys.

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Inventors:
Kurt R  th,
Otto M  ller,
Otto Ewald Dietzel,
by Pierce & Scheffler,
Attorneys.

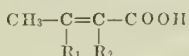
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INTERPOLYMERIZATION PRODUCTS

Werner Starck, Hofheim, and Kurt Billig, Frankfurt am Main-Hoechst, Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 4, 1941

The present invention quite generally relates to new and valuable interpolymerization products which may be obtained by polymerizing a mixture of about 90 per cent to about 98 per cent of a vinyl ester of an organic carboxylic acid with about 2 to about 10 per cent of a compound of the following formula:



wherein R₁ and R₂ stand for a substituent of the group consisting of hydrogen, methyl and chlorine. These interpolymerization products are a valuable new type of synthetic resins the properties of which are not inferior, as might be expected, but are superior to those of the polyvinyl esters themselves. For instance the softening point of the interpolymerization product of vinyl acetate and crotonic acid ester is not decreased, as compared with that of polymerized vinyl acetate, but increased, that is, the resistance to heat is improved. Furthermore the interpolymerization product is more resistant to water and atmospheric conditions than is the polymerization product from polyvinyl acetate alone. Since crotonic acid and its derivatives containing free carboxylic acid groups are not capable of being polymerized alone, the present process involves the great advantage that the polymerization product is always a complete interpolymerization product for none other than the interpolymerization products can be formed; whereas, in the case of interpolymerization products of two components each of which can be polymerized alone, uniformity of product cannot be obtained unless the most favorable conditions are carefully observed, or even then.

The new artificial resins are insoluble in water, whereby they are advantageously distinguished from those interpolymerization products which are obtainable from mixtures containing more than 10 per cent of crotonic acid. Such products prepared from large portions of crotonic acid have at least a swelling power in water. When being mixed with alkalies, such as potassium hydroxide, sodium hydroxide, lithium hydroxide and ammonium hydroxide and potassium carbonate, sodium carbonate, lithium carbonate and ammonium carbonate, or with organic nitrogen bases, such as monomethylamine, dimethylamine and trimethylamine and monoethylamine, diethylamine and trimethyl amine, ethanolamine or triethanolamine, the new resins yield salts which are soluble in water. The aqueous salt solutions thus obtained are particularly valuable for in-

dustrial purposes, since, on drying, they yield films which, if ammonia or bases volatile at room temperature are used as salt-forming components, become resistant to water already at room temperature. The films obtained from other salts may be rendered resistant to water by heating. By using a quantity of crotonic acid of less than 2 per cent for the preparation of interpolymerization products, there exists the danger that the interpolymerization products do no longer sufficiently dissolve or at least swell in aqueous alkalies.

The polymerization is performed by the known methods of polymerizing particularly those applied to vinyl esters. There may be present a solvent or an indifferent diluent; the polymerization may also occur in an emulsion. In order to accelerate the reaction, heat or light may be used as well as a catalyst, for instance a peroxide. It is suitable to apply less than about 1 mol of crotonic acid or the derivative thereof per about 1 mol of the readily polymerizing ester.

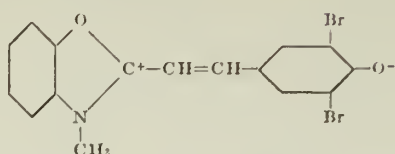
As vinyl esters of organic carboxylic acids there may be used: vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl chloracetate, vinyl butoxacetate, vinyl benzoate, vinyl stearate. As the other component there may be applied: crotonic acid, beta-chlorcrotonic acid, alpha-methylcrotonic acid, beta-methyl crotonic acid.

There may likewise be polymerized two, three or more of the vinyl esters named above in mixture with the crotonic acid or one of the derivatives thereof named above.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts are by weight:

(1.) A solution of 10 parts of crotonic acid in 90 parts of vinyl acetate to which 0.5 part of benzoyl peroxide has been added is caused to run in the course of 4 hours into a glass flask provided with a reflux condenser and a feed vessel and heated in a water bath to 80° C-85° C. The mass becomes more and more viscous while a strong reflux takes place. After all of the solution has been introduced, the whole is further heated for 12 hours. The entire content of the flask has solidified to a colorless, hard block. After cooling the glass flask is broken and the block is mechanically comminuted to small pieces. The product dissolves in organic solvents, such as methanol or ethyl acetate to form a highly viscous solution; furthermore it dissolves in aqueous alkalies, such as ammonia or sodium carbonate, with formation of salt.

tate in methanol. A dyestuff of the following constitution crystallizes:

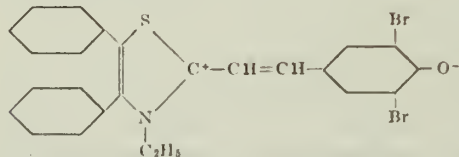


Color of the methanolic solution: orange-yellow.

Coloring of the acetate silk: orange-red.

Example 2

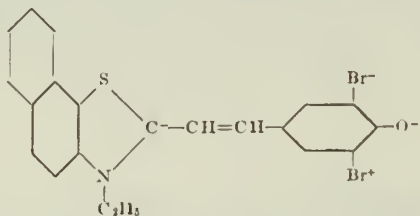
4 g of 2-methyl-4,5-diphenylthiazazole ethyliodide and 3 g of 3,5-dibromo-4-hydroxybenzaldehyde are dissolved while boiling in a mixture of 20 cc pyridine and 20 cc of alcohol. The mass is then mixed with 2 cc of piperidine and heated to 90° C for 1 hour. On cooling the following dyestuff crystallizes out:



Color of the methanolic solution: red-violet.
Coloring of the acetate silk: red.

Example 3

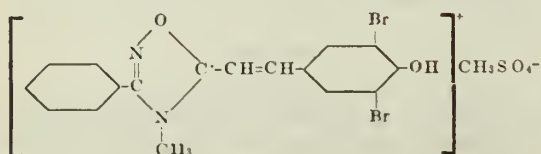
A mixture of 4.5 g of 2-methyl-β-naphthothiazole ethyliodide, 3 g of 3,5-dibromo-4-hydroxybenzaldehyde, 20 cc pyridine, 20 cc of propanol, and 2 cc of piperidine is boiled for half an hour. A dyestuff of the following formula crystallizes out:



Color of the methanolic solution: red-violet
Absorption maximum: 550 mμ
Color of the pyridine solution: blue-violet
Absorption maximum: 590 mμ,
Coloring of acetate silk: intensive red-violet.

Example 4

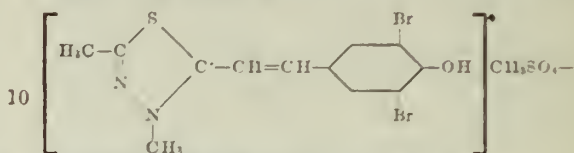
A mixture of 1.5 g of 2-methyl-4-phenyl-iso-furodiazole and 1 cc of dimethylsulfate is heated to 120° C for half an hour. The mass is then mixed with 2 g of dibromohydroxybenzaldehyde and kept at this temperature for half an hour. The dyestuff forms yellow crystals which dissolve in a solution of methanol and some drops of pyridine with a dark yellow color. The formula is as follows:



Absorption maximum: about 500 mμ
Coloring of the acetate silk: yellow-orange.

Example 5

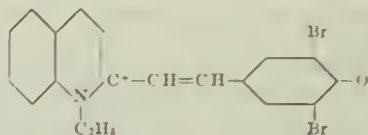
An orange-red dyestuff of the following constitution is obtained by means of 2,5-dimethylthiazole in an analogous manner to that as described in Example 4:



Coloring: orange-red.

Example 6

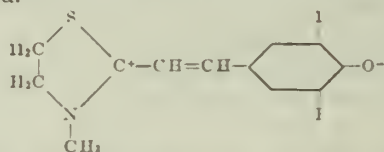
A mixture of 3 g of quinoldine ethyliodide, 3 g of dibromohydroxybenzaldehyde, and 10 cc of pyridine is boiled for half an hour. A violet-red dyestuff of the following constitution crystallizes out:



Color of the solution: red-violet.
Absorption maximum: about 550 mμ.

Example 7

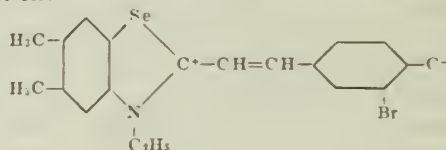
A mixture of equimolecular amounts of 2-methylthiazoline methyliodide and 3,5-diiodo-4-hydroxybenzaldehyde and some drops of pyridine are melted together at 120° for 1 hour. The mass thus prepared is then dissolved in methanol. On addition of an ammonia solution of 1% strength a dyestuff of the following formula is obtained.



Color of the methanolic solution and coloring: pure-yellow.

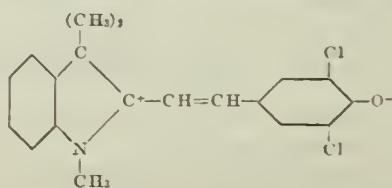
Example 8

5 g of 2,5,6-trimethylbenzelenazole ethyliodide are condensed with 5 g of 3-bromo-4-hydroxybenzaldehyde in the presence of 10 cc of pyridine. One obtains a red dyestuff of the following constitution:



Example 9

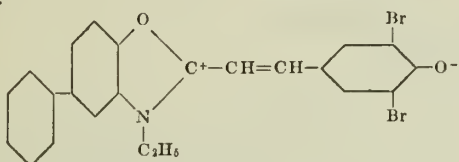
5 g of 1,2,3,3-tetramethylindoliniumperchlorate and 6 g of 3,5-dichloro-4-hydroxybenzaldehyde are condensed by heating at 110° C for half an hour to form a violet-red dyestuff of the following constitution:



Coloring of acetate silk: intensive red.

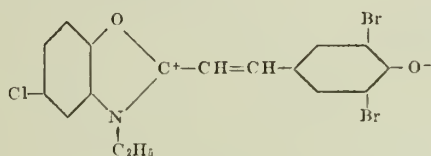
Example 10

A mixture of 7 g of 2-methyl-6-phenylbenzoxazole and 5.2 g diethylsulfate is heated at 120° C in an oil bath for one hour. 9 g of 3,5-dibromo-4-hydroxybenzaldehyde and 3 cc of pyridine are then added to the mass and the whole is heated at 120° C for a further hour. Finally the melt is dissolved in 200 cc of a methanolic solution of sodium acetate of 12.5%. On standing an orange-red dyestuff of the following formula crystallizes out:



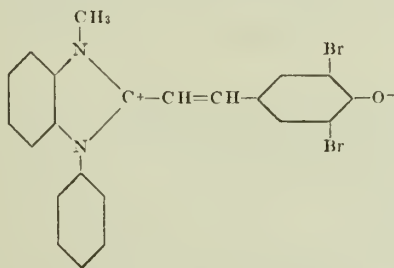
Example 11

On replacing 2-methyl-6-phenylbenzoxazole in Example 10 by 2-methyl-6-chlorobenzoxazole an analogous dyestuff likewise yielding an orange-red solution and coloring and having the following formula is obtained:



Example 12

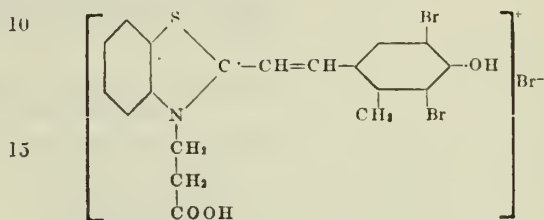
5 g of 2-methyl-1-phenyl-benzimidazole and 5 cc of dimethylsulfate are heated at 140° C in an oil bath for one hour. 8 g of the sodium salt of 3,5-dibromo-4-hydroxybenzaldehyde (obtained by precipitating an aqueous alkaline solution of the dibromohydroxybenzaldehyde with a concentrated solution of sodium hydroxide in excess), 20 cc of pyridine and 5 cc of piperidine are then added thereto and the whole is subsequently heated at 110° C for 6 hours. After acidifying the mass with diluted acetic acid; the precipitated dyestuff is sucked off, dissolved in methanol and slowly mixed with ether. Orange-red crystals dissolving in pyridine with an orange-red color are obtained. The dyestuff has the following formula:



Absorption maximum in pyridine: 525 μ
 Color of the methanolic solution: yellow
 Absorption maximum: 460 μ
 Coloring: pure-yellow.

Example 13

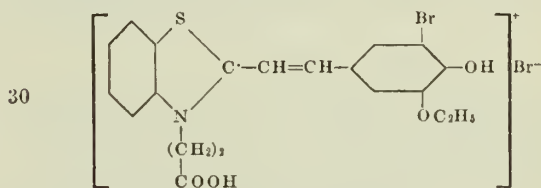
A mixture of 5 g of 2-methylbenzthiazole- β -propionyl bromide, 4 g of 2-methyl-3,5-dibromo-4-hydroxybenzaldehyde and 2 cc of pyridine is heated at 105° C for half an hour. The melt is then rubbed together with propanol and the resulting dyestuff sucked off. It is of the following formula:



Color of the solution and coloring; carmine red.

Example 14

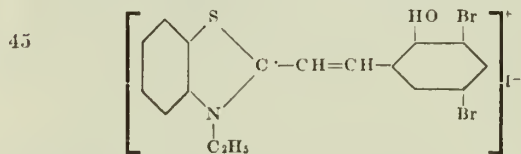
5 g of 2-methylbenzthiazole- β -propionyl bromide and 5 g of 3-bromo-4-hydroxy-5-ethoxybenzaldehyde are condensed in the manner as described in Example 13 to form a dyestuff of the following constitution:



Color of the solution: deep-red.

Example 15

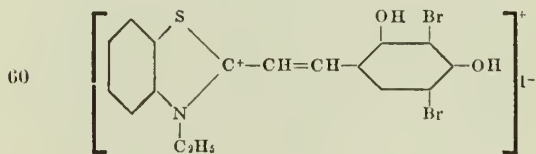
10 g of 2-methylbenzthiazole ethyliodide and 10 g of 3,5-dibromosalicylaldehyde are condensed with 20 g of pyridine by heating for half an hour. The solution is then mixed with 5-times its weight of propanol and caused to crystallize out. The dyestuff thus obtained has the following formula:



Coloring of wool and acetate silk: blue-violet.

Example 16

When in Example 15 3,5-dibromoresorcyaldehyde is used instead of 3,5-dibromosalicylaldehyde, a dyestuff yielding violet colorings and having the following constitution is produced:



OSKAR RIESTER.

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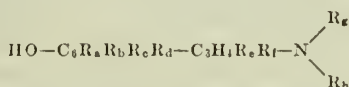
METHOD FOR PREPARATION OF OXY-PHENYL-AMINO-PROPANE AND ITS DERIVATIVES

Fritz Külz, Frankfurt/Main, Germany; vested in the Alien Property Custodian

No Drawing. Application filed November 19, 1941

This invention refers to the preparation of a class of chemical compounds which are chemically denominated as oxyphenyl-amino-propenes. These compounds comprise not only the individual compound, namely the oxyphenyl-amino-propane itself which exists in two isomers namely the 1-oxyphenyl-2-amino-propane and the 2-oxyphenyl-1-amino-propane but also a number of substitution products. Thus, at least one of the hydrogen atoms of the phenyl rest may be substituted by a lower molecular alkoxyl group or by a lower molecular alkyl group or another lower molecular radical. Furthermore, in the propane chain, at least one of the hydrogen atoms may be substituted by a lower molecular alkyl radical. Finally, in the amino group, at least one of the hydrogen atoms may be substituted by a lower molecular alkyl or alkylene radical or by an aralkyl, aralkylene, aryl, cycloalkyl, cycloalkylene radical or the tetramethylene or the pentamethylene rest.

Accordingly the compounds have the general formula:



Anyone of the radicals designated by R_a to R_d may be, in optional sequence, either the hydrogen atom or the alkoxyl group or the alkyl group. Preferably the alkoxyl groups and the alkyl groups are the lower homologues, and contain at most four C atoms. The methyl, the ethyl, propyl, isopropyl, butyl group and the corresponding alkoxy-groups are examples of these radicals.

Any one of the radicals denominated as R_e and R_f may be either hydrogen or a lower molecular alkyl, preferably with at most four C atoms, for example methyl, ethyl, propyl, isopropyl, butyl etc.

R_g and R_h mean hydrogen or alkyl, or alkylene or aralkyl or aralkylene or aryl or cycloalkyl or cycloalkylene or the tetramethylene or the pentamethylene rest or another polymethylene rest by which one or both of the free nitrogen valences may be bound. The alkyl or alkylene group contains preferably not more than six C atoms, the aralkyl and aralkylene radicals are the phenyl group with a saturated or unsaturated side chain of at most four C atoms, and the cycloalkyl and cycloalkylene groups are respectively the fully and partially hydrogenated phenyl group, in which one or more hydrogen atoms are substituted or not by methyl, ethyl, propyl, isopropyl or butyl or similar low molecular alkyls.

Hitherto compositions of the type referred to have been prepared from the corresponding alkoxy-compounds for example from the methoxy-compound, by splitting off alkyl (methyl)

and converting thus the said alkoxyl group into the hydroxyl group.

According to the present invention, as initial substances the oxyphenyl-propylene otherwise denominated as oxy-allyl-benzol and its substitution products are used which often are ingredients of ethereal oils, for instance the chavicol or the eugenol, or can be easily obtained by synthesis, for example the 3,5-dimethoxy-4-oxy-allyl-benzol or the 3,5-diethoxy-4-oxy-allyl-benzol. All these initial substances are of the general formula:



in which R_a to R_d may be either hydrogen or a lower molecular alkoxyl group or a lower molecular alkyl group and in which $\text{C}_3\text{H}_3\text{R}_e\text{R}_f$ may be the propylene (allyl) radical or a mono- or bi-alkyl substituted isopropylene with the double bond at the free end of the chain.

The initial substance is treated by hydrogen halogenide which is attached to the double bond of the allyl radical. The obtained products are converted into the amines by treatment with ammonia or a primary or a secondary amine; accordingly R_g and R_h may be either hydrogen or an alkyl, an alkylene, an aralkyl, an aralkylene, an aryl, a cycloalkyl or a cycloalkylene group. R_g and R_h may also be linked together in an annular configuration for example by tetramethylene or pentamethylene or another polymethylene. Examples of substances capable of this reaction are ammonia or primary amines for example methyl amine or ethylamine or aniline or toluidine or xylydine or their partially or totally hydrogenised derivatives or benzylamine or secondary amines like dimethyl amine or diethyl amine or methyl-ethyl-amine or methyl-isopropyl amine or diphenyl amine or methylaniline or dibenzylamine or piperidine or pyrrolidine.

As to this addition of hydrogen halogenide to oxy-phenyl-allyl compounds, it could not be foreseen that the addition products were stable enough since corresponding addition products of the alkoxyl type, namely of the safrol, the eugenol methyl ether and the anethol, were described as very unstable and inclined to decomposition by splitting off hydrogen halogenide, even when they are distilled under reduced pressure. (cf. German Patent 274,350) Hence it was surprising that the addition products obtained according to the invention are sufficiently stable, in spite of the free hydroxylic group of the phenyl radical which generally is most reactive and could not be expected to remain indifferent in this reaction.

Contrary to this expectation it could be stated that not only the addition of hydrogen halogenide takes place without difficulties but that it is also possible to distil the resulting addition products under reduced pressure. It was surprising,

too, that the free hydroxylic group does not prevent or disturb the double decomposition of the addition product with ammonia or a primary or secondary amine.

Thus, according to the invention, it is possible to obtain oxyphenyl-alkylamines from easily available or obtainable products, merely by two steps namely by the addition of hydrogen halogenide and the subsequent substitution of the amino group in lieu of the halogen.

The initial substances which correspond to the general formula mentioned above may consist of different isomers but the hydroxyl group attached to the phenyl rest must be in the meta or para position to the allyl rest.

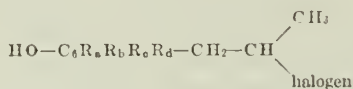
As to the hydrogen halogenide there may be used in the process either hydrochloric acid or hydrobromic or hydroiodic acid while hydrofluoric acid is of less importance particularly since the working with this substance is rather troublesome.

These acids are preferably employed in concentrated form and spontaneous heating should be prevented by suitable means for instance cooling down to the freezing point. To avoid undesired reactions or decompositions the intermediate product should be freed from the exceeding acid by suitable means for instance by washing with dilute alkali carbonate solution. After careful exsiccation the product may be further purified by distillation or rectification or any other suitable means before it is transformed into the amine by treatment with ammonia or a primary or secondary amine.

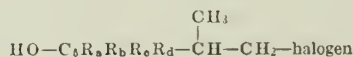
This second step of the process may be accelerated by increased temperature, for instance by boiling.

The final products may be purified by dissolving them in a dilute acid, and by extracting them with a suitable solvent, for instance ethylic ether, which dissolves the neutral ingredients. The product thus obtained may be distilled and rectified. By this operation the exceeding amine can be separated. In lieu of the rectification or additionally the purification may be obtained by crystallization as hereinafter set out.

The final product, i. e. the oxy-phenyl-amino-propane or its derivatives, is obtained in two different isomers, namely the 1-oxyphenyl-2-amino-propane and the 2-oxyphenyl-1-amino-propane; since, according to the conditions of working, the intermediate product corresponding to the formula



or its chain-substituted derivative is more or less transformed by the so-called pinacoline interchange to a substance of the following formula



and its chain-substituted derivative respectively. The last mentioned isomer has often merely the character of an impurity and does not much impair the properties of the first mentioned compound. In cases where pure products and the isolation of the single isomer are desired this can be achieved by fractional crystallization, either of the intermediate product or of the final product when these are solid substances. When, however, the final product is a liquid it may be converted into a salt from which the isomers are separated by fractional crystallization. These

salts are formed by mere addition of anorganic or organic acids; hydrochloric acid, hydrobromic acid, hydroiodic acid, sulphonic acid, perchloric acid and the corresponding acids of the other halogens, low molecular monobasic fatty or aromatic acids for example acetic acid or picric acid, oxyacids like lactic acid, and dibasic acids like oxalic, malonic, succinic acid and higher basic acids like citric acid, are found to be suitable for this purpose.

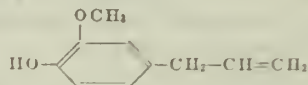
The salts of the two isomers show different solubility within suitable solvents so that it is possible to separate the isomers by mere crystallization.

The final products are of therapeutical value.

Further particulars of the invention may be seen from the following examples. The amounts are by weight.

EXAMPLE 1

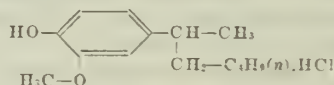
To one part of eugenol



four parts of hydrochloric acid (sp. gr.=1.19) are added; the mixture is mechanically shaken during twenty-four hours at room temperature. Then the oily layer which is of dark green colour and consists mainly of the reaction product, is separated, washed with water, alkali bicarbonate solution and again with water and finally carefully dried by means of calcium chloride. The dried reaction product is then distilled under reduced pressure. The boiling point is 152° to 155° C/12 mm. The distilled product contains 16.90 percent of chlorine which for the product $\text{C}_{10}\text{H}_{13}\text{O}_2\text{Cl}$ is calculated to 17.67 percent.

10 parts of this addition product is then boiled for five hours under reflux with a solution of 10 parts of n-butylamine in 20 parts by volume of anhydrous ethyl alcohol. Then the alcohol and the exceeding amine is distilled off under reduced pressure; the residue is acidified with dilute hydrochloric acid and then extracted with ethylic ether to remove neutral ingredients. Then ammonia is added to obtain the free amines which are extracted by ether. The ethereal solution is dried with sodium sulphate, whereupon the ether is vaporized. The residue which consists of the free amines is distilled under highly reduced pressure (0.05 mm mercury). The fraction boiling between 120° and 125° C/0.05 mm is dissolved in ethylic ether, and an ethereal solution of hydrochloric acid is added. The obtained chlorhydrate has the unsharp melting point of 128 to 132° C.

By repeated recrystallization from methanol a chlorhydrate of the melting point of 184 to 185° C was obtained which was identified as the 2-(3-methoxy-4-oxyphenyl)-1-n-butylamino-propane-chlorhydrate of the following formula $\text{C}_{14}\text{H}_{23}\text{O}_2\text{N} \cdot \text{HCl}$

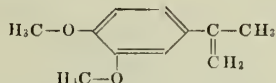


Analysis:					
Calculated.....	C 61.39	H 8.81	N 5.11		
Found.....	C 61.28	61.34	H 8.72	8.75	N 5.29

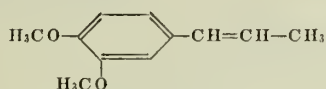
For the purpose of identification the product was thoroughly methylated at the oxygen and nitrogen by treatment with dimethyl-sulphate and alkali; subsequently the quaternary salts are decomposed by Hofmann's method, and resulted in a product of the melting point 36-37°C. This product was identified as the pseudo eugenol-

methyl ether by comparison with a product obtained according to the method of Béhal and Tiffeneau (Bull. Soc. Chim. France IV, 3,732 (1908) and by the mixing text with this product.

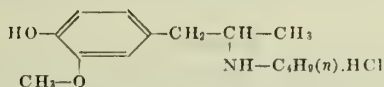
The formula of the pseudo eugenol methyl ether is:



On concentration of the mother lye or on addition of ethylic ether an isomeric chlorhydrate is obtained which on repeated recrystallization shows the constant melting point of 135° to 136° C. This product treated by Hoffmann's method mentioned above yields the iso-eugenol methyl ether of the formula



which was identified by the formation of the corresponding pseudo-nitrosite (m.p. 107° C) and the mixing text with a product obtained by the method of Angeli (Ber. 24, 3996 (1891) and of Wallach (Liebigs Ann. 332, 335 (1904)). The obtained chlorhydrate (m. p. 135° to 136°) is therefore the 1-(3-methoxy-4-oxyphenyl)-2-n-butylamino-propane-chlorhydrate of the formula



Analysis:
Calculated: C₁₄H₂₃O₂N.HCl mol. wt. 273.7
C 61.39 H 8.84 N 5.11
Found: C 61.25, 61.42 H 8.76, 8.75 N 5.05, 5.07

EXAMPLE 2

34 parts hydrobromic acid (66 percent) are slowly added to 15 parts eugenol while a vigorous agitation is maintained and the reaction temperature is decreased to 0° C by means of external cooling with a freezing mixture. Subsequently the reaction product is agitated or shaken for five to six hours and cooled with ice. Then one adds water, extracts with chloroform, washes the chloroformic solution with water, dilute sodium carbonate solution and again with water, and dries with calcium chloride. After vaporisation of the chloroform the addition product of hydrobromic acid to eugenol remains as an oily residue which can be distilled under reduced pressure without decomposition. B. p. 163°/10 mm or 127 to 128°/0.5 mm.

This addition product is slowly poured into the fourfold amount of ethyl alcohol saturated with gaseous ammonia, whereby the ammonium salt is formed as a crystalline precipitate. Subsequently one shakes mechanically for two days, whereby the mixture becomes less consistent, and adds ethylic ether and filters off the precipitate.

This precipitate is kept during a sufficient time in a vacuum exsiccator which is filled with sulphuric acid, then dissolved in the ten-fold amount of water and boiled and bleached with animal coal. After filtration, ammonia is added to alkaline reaction. A basic substance is separated in crystalline condition which, after fractional distillation under reduced pressure (b. p. 167°/10 mm) shows the melting point of 173° C. The corresponding chlorhydrate recrystallised from a

mixture of methanol and ethylic ether melts at 267° C.

Analysis:

Calculated for: C₁₀H₁₅O₂N mol. wt. 181.1
C 66.25 H 8.35 N 7.73
Found: C 66.45 H 8.37 N 7.54, 7.73

The filtrate left after the separation of the precipitate is evaporated, the residue dissolved in ethylic ether and the ethereal solution dried with sodium sulphate; then the ether is vaporized, and the residue distilled under reduced pressure. The distillate (b. p. 172° C/12 mm) may be converted into the corresponding chlorhydrate which after crystallization from a mixture of methanol and ethylic ether, melts at 229° to 230° C. The free amine melts at 147° to 148° C.

Analysis:

Calculated for: C₁₀H₁₅O₂N mol. wt. 181.1
C 66.25 H 8.35 N 7.73
Found: C 66.33 H 8.31 N 7.51

Which of these both isomers corresponds to the 1-(3-methoxy-4-oxyphenyl)-2-amino-propane and which to the 2-(3-methoxy-4-oxyphenyl)-1-amino-propane was not verified.

EXAMPLE 3

To 34 parts of n-butylamine 19.5 parts of the intermediate product obtained in the first step of the reaction described in the preceding example dissolved in anhydrous alcohol, are slowly added. The mixture is boiled for three hours under reflux. After vaporisation of the alcohol and the excess of the amine one adds hydrochloric acid, and extracts with ethylic ether to remove neutral substances. From the hydrochloric solution the amine is freed in the usual manner, and distilled under highly reduced pressure (b. p. 120° to 125°/0.05 mm). The distillate is dissolved in ethylic ether and an ethereal solution of hydrochloric acid is added whereby the corresponding chlorhydrate is precipitated from which the single isomers may be obtained by crystallization from methanol. The isomers melt at 184° to 185° and 135° to 136° respectively, and are identical with those obtained according to example 1. For the separation of the isomers, besides other anorganic and organic salts, the neutral salts of the succinic acid are particularly suitable. For this purpose the distilled amine is dissolved in a small amount of alcohol and mixed with succinic acid in the molecular relation of 2 to 1; then the solution of the salts is evaporated, and the residue is recrystallized from water. Firstly a succinate melting at 143° to 145° crystallises which after double recrystallization melts constantly at 150° to 151° C. This compound is the neutral succinate of the 1-(3-methoxy-4-oxyphenyl)-2-n-butylamino-propane which contains two molecules of water of crystallization, and is soluble in water with neutral reaction against phenol-phthaleine as indicator.

After considerable evaporation of the aqueous mother lye there crystallises the succinate of the isomeric 2-(3-methoxy-4-oxyphenol)-1-n-butylamino-propane which, after recrystallization from water melts constantly at 99° to 100°. It contains 5 molecules of water of crystallization and is soluble in water with neutral reaction.

Analysis:

Calculated for: (C₁₄H₂₃O₂N)₂.C₄H₆O₄ mol. wt. 592.4
C 64.82 H 8.85
Found: C 64.34 H 9.04

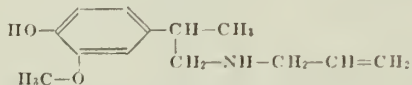
EXAMPLE 4

10 parts of the addition product of hydrobromic acid to eugenol obtained in the first step of the process described in example 2 are heated for two hours on the water-bath and under pressure with 10 parts of allyl amine dissolved in 25 parts by volume of anhydrous alcohol. The reaction product is obtained according to example 1, and distilled under reduced pressure (b. p. 174° to 177°/12 mm). The distillate which crystallises at ordinary temperature melts unsharply at about 150 to 151° C. The product was analysed without separation of the isomers.

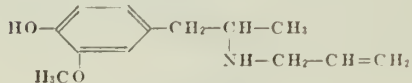
Analysis:

Calculated for	$C_{15}H_{17}O_2N$ mol. wt. 221.1
Found	C 70.55 H 8.61 N 6.33
	C 70.58 H 8.59 N 6.39

Formulas



and



EXAMPLE 5

To 12.2 parts of the intermediate product obtained by the first step of the process described in example 2 and dissolved within 20 parts by volume of anhydrous alcohol, 22 parts of isoamyl-amine are slowly added. A temperature of 70° to 80° C is maintained for 2 to 3 hours. Then the alcohol and the excess of the amine is distilled off. By the same treatment described in example 1 a reaction product is obtained which distills under reduced pressure at 187° to 189°/14 mm. The yield is 78 percent of the theory. For the purpose of separating the distillate into the isomers it is converted into the chlorhydrate derivative which is fractionally crystallised from a mixture of methanol and ether. The product which is more difficultly soluble melts constantly at 210° C.

Analysis:

Calculated for	$C_{15}H_{21}O_2N \cdot HCl$ mol. wt. 287.7
Found	C 62.57 H 9.11 N 4.57
	C 62.50 H 9.04 N 4.81

The product which is more easily soluble melts at 156° C.

Analysis:

Calculated for	$C_{15}H_{23}O_2N \cdot HCl$ mol. wt. 287.7
Found	C 62.57 H 9.11 N 4.87
	C 62.58 H 9.06 N 4.91

EXAMPLE 6

30 parts of piperidine are added according to example 3 to a solution of 20 parts of the intermediate product obtained in the first step of the process described in example 2. After the reaction is completed the crystallised piperidine chlorhydrate is separated from the alcoholic solution by filtration. The alcohol and the excess of the piperidine are vaporised under reduced pressure and the residue treated as in the foregoing examples. On concentration of the ethereal solution firstly an isomer crystallises having the unsharp melting point of 130° to 131° which, after recrystallization from alcohol melts constantly at 131° to 132° C. The corresponding picrate melts constantly after recrystalliza-

tion from alcohol at 182° to 183° C., the corresponding chlorhydrate at 213° to 214° C.

Analysis:

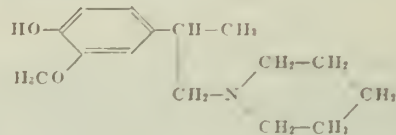
Calculated for	$C_{15}H_{21}O_2N$ mol. wt. 249.2
Found	C 72.23 H 9.31
	C 72.26 H 9.17

The ethereal mother lye is completely evaporated, and the residue is heated under reduced pressure to remove the remaining traces of piperidine. Then the residue is dissolved in a small amount of alcohol; by repeated crystallization from alcohol a further isomer is obtained which melts at 89° to 90° and whose picrate and chlorhydrate melt at 130° to 132° and 150° to 152° respectively.

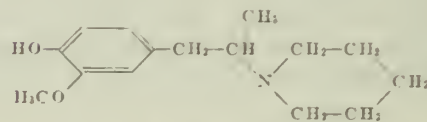
Analysis:

Calculated for	$C_{17}H_{23}O_2N$ mol. wt. 249.2
Found	C 72.23 H 9.31
	C 72.25 H 9.29

The formulas are:



and



EXAMPLE 7

16 parts of pure chavicol are treated according to example 2 with 44 parts hydrobromic acid (66 percent). The obtained addition product boils under highly reduced pressure at 110° to 115°/0.5 mm.

Analysis:

Calculated for	$C_{15}H_{17}O \cdot Br$ mol. wt. 215.0
Found	Br 37.17
	Br 37.04

10 parts of this addition product are boiled for three hours and a half under reflux with 17 parts of n-butyl amine dissolved in 20 parts by volume of anhydrous alcohol. The reaction product is purified like in the foregoing examples, and distilled under highly reduced pressure (b. p. 167° to 170° C/0.05 mm).

For the purpose of separating the isomers the distillate is dissolved in ethylic ether and precipitated with lactic acid. The obtained lactates are crystallised from a mixture of anhydrous alcohol and ethylic ether. The crystallised less soluble lactate melts at 135° to 136° C.

Analysis:

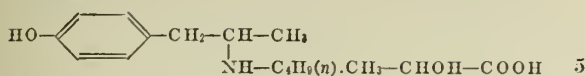
Calculated for	$C_{17}H_{23}ON$ mol. wt. 297.2
Found	C 64.60 H 9.16
	C 64.68 H 9.12

From the mother lye the amine is preferably freed and converted into the bromhydrate which is crystallised from a small amount of water. From the part which is easily soluble in water the free amine is obtained which is subsequently converted into the lactate which is recrystallised from a mixture of alcohol and ether (m. p. 94° to 95° C). It contains one molecule of water of crystallization of which one half is split off under highly reduced pressure.

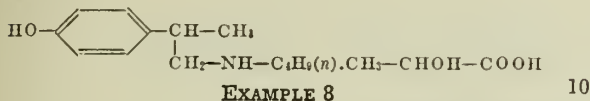
Analysis:

Calculated for	$C_{15}H_{25}ON \cdot C_5H_7O_2 \cdot \frac{1}{2} H_2O$ mol. wt. 306.2
Found	C 62.71 H 9.22
	C 62.30, 62.38 H 9.21, 9.22

The two isomers correspond to the following formulas:



and



47 parts of 3,5-dimethyl-4-oxy-1-allyl-benzol are treated with hydrobromic acid according to example 2, but maintaining the temperature at about +3° C to prevent congealing of the reaction mass. The purified reaction product boils without decomposition at 165° to 168°/11mm. At ordinary temperature it becomes solid.

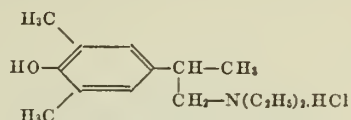
To 10 parts of this addition product which are dissolved in 20 parts by volume of anhydrous alcohol, 10 parts of diethyl amine are added whereby a spontaneous increase of temperature is observed. After twelve hours the reaction product is purified as described in the foregoing examples. The mixed isomers of the amines boil at 157° to 160°/10 mm. By addition of hydrochloric acid dissolved in ether the chlorhydrates are obtained whose less soluble part crystallised from methanol, melts at 217° C.

Analysis:

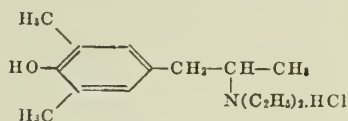
Calculated for-----	$\text{C}_{15}\text{H}_{21}\text{ON} \cdot \text{HCl}$	mol. wt. 271.7
Found-----	C 66.26 H 9.64	
	C 66.30 H 9.63	

The more soluble isomer was not isolated.

The isomers correspond to the following formulas:



and



EXAMPLE 9

30 parts of utmost concentrated hydroiodic acid are added to 10 parts of eugenol at room temperature and under permanent agitation. Subsequently the reaction mass is agitated for five hours and then mixed with water. The separated oily layer is diluted with chloroform, and this solution washed with sulphurous acid, water, a solution of sodium bicarbonate and again with water and finally dried with calcium chloride. The solution is evaporated. After the vaporisation of unchanged eugenol the residue boils under highly reduced pressure at 130° to 135° C/0.3 mm.

The further operation corresponds to the method described in example 1, and finally two isomers of n-butylamino-derivatives are obtained.

FRITZ KÜLZ.

ALIEN PROPERTY CUSTODIAN

QUATERNARY AMMONIUM COMPOUNDS AND METHODS OF PRODUCING SAME

Winfried Hentrich, Dusseldorf-Reisholz, Wilhelm Kaiser, Dessau/Anhalt, and Werner Reuss, deceased, late of Dusseldorf-Benrath, Germany, by Carl-Heinz Winkler, administrator, Dusseldorf, Germany; vested in the Alien Property Custodian

No Drawing. Application filed January 16, 1942

The producing of amino-carboxylic acid amides or -esters including those which in the amido- or in the ester group contain at least one lipophile radical, or residue, is not new. It can be performed in letting react ammonia or amines upon halogenated carboxylic acid amides or -esters, but the converting of amino-carboxylic acid halogenides with alcohols or amines respectively is likewise practicable.

Now it has been found that valuable nitrogenous compounds are obtainable in converting such amino-carboxylic acid amides or -esters containing on the amino-nitrogen or in the ester group at least one lipophile radical, into quaternary ammonium compounds.

The amino-carboxylic acid amides or -esters which may be applied as initial materials for the present method, are of the general formula $R_1R_2N.R_3CO.X.R_4$. In this formula R and R mean hydrogen or any hydrocarbon radicals which also conjointly may form with the nitrogen-atom a heterocyclic ring; R_2 means a bivalent hydrocarbon radical; X represents NR_4 (R_4 =hydrogen or any hydrocarbon radical) or O, whilst R_3 is to be a hydrocarbon radical with no less than 6 carbon atoms.

R and R_1 may e. g. be formed of methyl-, ethyl-, propyl-, allyl- groups and the like, or they may also belong to a piperidine- or pyrrolidine ring. Further they may be formed of a benzyl-, furfuryl-radical and the like. The several compounds are similar, and to a substantial extent equivalents, in that they all have the important tri-valent N atom. R_2 may be represented by e. g. an ethylene-, phenyl ethylene-, propylene- or butylene radical and the like. R_3 may be formed of a higher molecular hydrocarbon radical containing no less than 6 C atoms of the aliphatic, cyclo-aliphatic, aromatic and fatty aromatic series such as a hexyl-, octyl-, decyl-, dodecyl-, cetyl-, octadecyl-, octadecenyl-, hydroxy-octadecenyl radical and the like. Moreover R_3 may be represented by a cyclohexyl radical, an alkylated cyclohexyl radical such as the p-dodecyl-o-methyl-cyclohexyl radical, a naphthenyl radical, an abietyl radical, a phenyl radical, an alkylated phenyl radical, a benzyl radical and the like. Those radicals may also contain hetero-atoms and hetero-atom groups such as oxygen, sulfur, nitrogen and the like. R_4 may be e. g. a radical of methyl, ethyl, propyl, allyl, butyl, benzyl, furfuryl, phenyl and the like.

Among the amino-carboxylic acid amides or -esters applicable as initial materials for the present invention there are to be considered e. g. di-

methyl-amino-acetic acid-octyl-amide, piperidino-acetic acid-octyl-amide, dimethyl-amino-butyric acid-dodecyl-amide, dimethyl-amino-acetic acid-undecylene-amide, dimethyl-amino-acetic acid-dodecyl-amide, di-ethyl-amino-acetic acid-cetyl-amide, β -dimethyl-amino- α -diethyl-propionic acid cetyl-ester, piperidino-acetic acid-dodecyl-benzyl-amide, dimethyl-amino-acetic acid-(p-dodecoxy)-phenyl-amide, and further the amino-acetic acid-dodecyl-amide, methyl-amino-acetic acid-cetyl ester, amino-propionic acid-dodecyl-benzyl amide and the like.

The converting of those compounds into quaternary ammonium compounds is accomplished by direct reaction of mineral acid esters of aliphatic, fatty aromatic, cyclo-aliphatic or heterocyclic alcohols such as alkyl-halogenides, e. g. methyl-chloride, methyl-iodide, allyl-bromide, octyl-bromide, hexadecyl-bromide, further the dimethyl sulfate, diethyl-sulfate, octyl-monosulfuric acid ester, benzyl chloride, furfuryl chloride, tetra-hydro-furfuryl chloride and the like.

The conversion by reaction between the amino-carboxylic acid amides or -esters, on the one hand, and the mineral acid esters, on the other hand, is performed while warming up and eventually in the presence of solvents or diluents.

Products, which may be obtained according to the prescribed process are e. g. dimethylamino-acetic acid-octylester-chloromethylate, dimethylamino-propionic acid-dodecylester-chloromethylate, dimethylamino-butyric acid-dodecylester-chloromethylate, dimethylamino-butyric acid-hexadecylester chloromethylate, dimethylamino-phenyl-acetic acid-dodecylester-chloromethylate, diethylamino-acetic acid-dodecylester-chlorobenzylate, dibutylamino-acetic acid-dodecylester-chlorobenzylate, difurfurylamino-acetic acid-dodecylester-chlorobenzylate, diallylamino-acetic acid-dodecylester-chlorobenzylate, piperidino-acetic acid-dodecylester-chlorobenzylate, pyrrolidino-acetic acid-dodecylester-chlorobenzylate, benzyl methyl-amino-acetic acid-dodecylester-chlorobenzylate, benzyl cyclohexylamino-acetic acid-dodecylester-chlorobenzylate, dimethylamino-acetic acid-decylester-chloromethylate, dimethylamino-acetic acid-octadecylester-chloromethylate, dimethylamino-acetic acid-octadecenylester-chloromethylate, dimethylamino-acetic acid-p-dodecyl-o-methyl-cyclohexyl-ester-chloromethylate, dimethylamino-acetic acid-naphtenyl-ester-chloromethylate, dimethylamino-acetic acid-dodecyl-ester-iodomethylate, dimethylamino-acetic acid-dodecylester-bromocetyl, dimethylamino-acetic acid-

dodecylester-chlorohexadecylate, dimethylamino-acetic acid-dodecylester-chlorofurfurylate, dimethylamino-acetic acid-dodecylester-chlorotetrahydrofurfurylate, dimethylamino-acetic acid-dodecylester-methosulfate.

Example 1

To 310 parts by weight of melted dodecylamide of the piperidino-acetic acid, 127 parts by weight of benzyl chloride are added while stirring and at a temperature of 50° C. After warming up from 50 to 60° C until the reaction is at its end, one allows cooling, whereby the melt solidifies to a crystalline mass. The thus obtained piperidino-acetic acid-dodecyl-amide-chlorobenzylate dissolves clear in water and the aqueous solution is much lathering. By re-crystallizing from Xylol the product can be obtained quite colourless (melting point 114° C). A similar compound is obtained in warming 7 parts by weight of piperidino-acetic acid-dodecyl-benzyl amide up to 50-60° C for about 2 hours together with 2.2 parts by weight of dimethyl-sulfate.

Example 2

19 parts by weight of piperidino-acetic acid-dodecyl-ester are warmed up to 80-90° C for 8 hours together with 13 parts by weight of benzyl-chloride. Then the mixture is dissolved in water and warmed, whereby the excess benzyl-chloride, which is floating in the form of oil on the surface of the solution, is to be separated off. After evaporating the solution liberated from the benzyl-chloride, we obtain the piperidino-acetic acid-dodecyl-ester-chlorobenzylate in the form of a powder. One may also substitute a mixture of fatty alcohol esters for the dodecyl-ester.

Example 3

270 parts by weight of dimethyl-amino-acetic acid-dodecyl-amide are warmed up to 50-60° C for several hours together with 127 parts of benzyl-chloride. The thus obtained crystalline mass may eventually be ground with a solvent (decahydronaphthalin) for purification. By sucking off the solvent we obtain the dimethyl-amino-acetic acid-dodecyl-amide-chlorobenzylate being a well crystallized substance (melting point 147 to 148° C) soluble clear in water.

In a similar manner we obtain the dimethyl-amino-acetic acid-(furfuryl-dodecyl-amide)-chloromethylate, piperidino-acetic acid(4-sec.-octyl-2-methyl-cyclohexyl-methyl-amide)-chlorobenzylate, (benzyl-methyl-amino)-acetic acid-(methyl-dodecyl-amide)-chloromethylate, dimethyl-amino-acetic acid (benzyl-dodecyl-amide)-chloromethylate and the like.

Example 4

270 parts by weight of dimethylamino-acetic acid-dodecylester are warmed with 127 parts by weight of benzylchloride for 8 hours at 90° C. The reaction mixture is freed from the excess of benzylchloride. We obtain the dimethyl-amino-acetic acid-dodecylester-chlorobenzylate, which is clear soluble in water.

Example 5

To 135 parts by weight of diethylamino-acetic acid-decylester 114 parts by weight of benzylchloride are added and warmed for 6 hours at 70-80° C. The thus obtained crystalline mass is purified by means of a solvent. The diethylamino-acetic acid-decylester-chlorobenzylate is obtained, which may be recrystallized from xylol.

Those quaternary ammonium compounds dis-

tinguish themselves, without counting their water-solubility and indifference to hardness-provokers of the water and to hydrolysing influences, not only by an excellent soap-like action, but also by a most remarkable disinfecting action upon e. g. the staphylo-coccus and the typhus bacillus.

Those compounds offer moreover the advantage of being obtainable in a generally very good crystalline form allowing an easy dosing and mixing with substratums. Besides this we can without difficulty obtain crystallizable products of such a purity as required e. g. for pharmaceutical purposes.

The aforesaid compounds may be applied either alone or mixed with other disinfecting media and eventually with an addition of diluents or stretching agents for the disinfection of commodities, medical instruments, textiles, linen, walls, tiles floors, implements, apparatus used in the alimentary and appetizing products industry, as well as for the disinfecting of animals and parts of the human body. Moreover they are apt for the preserving of perishable animal and vegetable goods such as pastes and sizes, furs, hides, skins and the like.

The quaternary amino-carboxylic acid-amides of the present invention are e. g. of the general formula $\text{Am.R'.CO.N.R''R'''}$. In this formula R'.CO means the radical of an aliphatic acid such as acetic acid, propionic acid and butyric acid. R''=hydrogen or any organic radical. R''' means a lipophile radical such as octyl-, nonyl-, decyl-, dodecyl-, tridecyl-, tetradecyl-, hexadecyl radical or the like. "Am" represents any quaternary ammonium group containing anion. The ammonium group may contain equal or mixed aliphatic, aromatic, aliphatic-aromatic or heterocyclic radicals. Of a particularly good disinfecting power are those compounds, which in the molecule e. g. in the quaternary ammonium group or on the amino-nitrogen contain a non-saturated organic radical such as the benzyl radical, the allyl-radical and the like.

The compounds of the present invention may therefore be applied also with alkaline or acid materials. Moreover they are of a good wetting-power by which the penetration into textiles and the spreading-out on soiled and stained surfaces is considerably enhanced. The efficiency and the mode of application of the compounds in question as disinfecting and preserving agents is shown by the following examples:

(a) A 0.01%-solution of (benzyl-methyl-amino)-acetic acid-dodecylamide-chloromethylate of the formula $(\text{CH}_3)_2(\text{C}_7\text{H}_7)\text{NCl.CH}_2\text{CO.NH.C}_{12}\text{H}_{25}$ kills completely, at 20° C a deposit of mycoderma within 15 minutes.

A 0.002%-solution of the same compound destroys completely at 20° C. a deposit of bacteria coli within 45 minutes.

A 0.0057%-solution of the same compound destroys completely, at 20° C, a deposit of staphylococcus aureus within 5 minutes.

Of a similar efficiency are also the compounds where the dodecyl-radical is replaced by an octyl-, decyl- or tetradecyl radical, as well as the mixtures of those bodies.

(b) A 0.01%-solution of dimethyl-amino-acetic acid-dodecyl-amide-chloromethylate of the formula $(\text{CH}_3)_3\text{NCl.CH}_2\text{CO.NH.C}_{12}\text{H}_{25}$ kills, at 20° C, a deposit of bacteria coli completely within 15 minutes.

A 0.014%-solution of the same compound destroys completely, at 20° C, a deposit of pyocyaneus within 5 minutes.

(c) A 0.005%-solution of dimethyl-amino-acetic acid (benzyl-dodecyl-amide)-chloromethylate of the formula



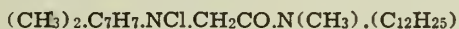
kills completely a deposit of bacteria coli within 15 minutes.

The same efficiency shows a 0.005%-solution of piperidino-acetic acid-dodecylamide-chloromethylate of the formula



(d) The 1%-solution of a mixture of 70 parts by weight of crystallized sodium-meta-silicate, 29 parts of crystallized tri-basic sodium-phosphate and 1 part of the dimethyl-amino-acetic acid-dodecyl-amide-chloromethylate (mentioned in example 2), kills completely, at 50° C, a deposit of mycoderma within 5 minutes. This solution may be heated for a rather long time and kept for several days without reducing its disinfecting power.

(e) A 0.005%-solution of (benzyl-methyl-amino)-acetic acid-(methyl-dodecyl-amide)-chloromethylate of the formula



kills completely, at 20° C, a deposit of bacteria coli within 30 minutes.

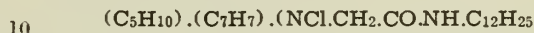
(f) A 0.01%-solution of dimethyl-amino-phenyl-acetic acid-dodecyl-amide-chloromethylate of the formula $(\text{CH}_3)_2\text{N}.\text{CH}(\text{C}_6\text{H}_5).\text{CO}.\text{NH}.\text{C}_{12}\text{H}_{25}$ destroys entirely, at 20° C, a deposit of bacteria coli within 15 minutes.

(g) A 0.002%-solution of benzyl-cyclohexyl-amino-acetic acid-dodecylamide-chloromethylate of the formula



kills completely, at 20° C, a deposit of bacteria coli within 45 minutes.

(h) 40 parts by weight of caustic soda, 30 of sodium-meta-silicate of the formula $\text{Na}_2\text{SiO}_3.5\text{H}_2\text{O}$, 19 parts by weight of calcined tribasic-sodium-phosphate, 10 of calcined sodium and 1 part of piperidino-acetic acid-dodecylamide-chlorobenzylate of the formula



are well mixed together. An aqueous solution of this mixture at the ratio of 0.25% kills entirely, at 50° C, a deposit of bacteria coli within 6 minutes.

(i.) A 0.01% solution of dimethylamino-acetic acid-dodecyl-ester-chloromethylate of the formula $(\text{CH}_3)_2\text{N}.\text{Cl}.\text{CH}_2.\text{CO}.\text{O}.\text{C}_{12}\text{H}_{25}$ kills, at 20° C, a deposit of bacteric coli completely within 20 minutes.

(k.) A 0.015% solution of piperidino-acetic acid-dodecyl-ester-chlorobenzylate of the formula $(\text{C}_5\text{H}_{10}).(\text{C}_7\text{H}_7).\text{N}.\text{Cl}.\text{CH}_2.\text{CO}.\text{O}.\text{C}_{12}\text{H}_{25}$ destroys entirely, at 20° C, a deposit of bacteric coli within 12 minutes.

(l.) A 0.005% solution of diethylamino-acetic acid-decylester-chlorobenzylate of the formula $(\text{C}_2\text{H}_5)_2.\text{N}.\text{Cl}.\text{CH}_2.\text{CO}.\text{C}_{12}\text{H}_{25}$ kills, at 20° C, a deposit of bacteric coli within 15 minutes.

The aqueous solutions of this mixture may be applied as excellent detergents of a simultaneous disinfecting action.

The present application is a division of application Serial No. 200,839½ filed April 8, 1938.

WINFRID HENTRICH.

WILHELM KAISER.

CARL-HEINZ WINKLER.

Administrator of the estate of Werner Reuss,
Deceased.

ALIEN PROPERTY CUSTODIAN

POROUS POLYVINYL CHLORIDE COMPOSITIONS

Herbert Berg and Martin Doriad, Burghausen,
Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 5, 1942

This invention relates to the production of porous polyvinyl-chloride compositions containing softeners.

It is known to produce porous compositions of polyvinyl compounds e. g. polystyrol or polyvinyl-chloride. In this process a mixture of a polyvinyl compound and a gas-producing substance is heated under a rapidly rising vacuum. The employed gas-producing substances, however, deteriorate the properties of the end products; besides there cannot be obtained a fine and homogeneous porosity by the rapidly rising vacuum. Therefore, products of this kind were not used in the arts till now.

Besides, it is known to produce porous compositions of polymethacrylic acid esters or luvikan by sintering these substances without softening agents in the form of powders or grains by heating them under a soft pressure or by softening them by employing solvents and then combining them under pressure. Since in the last and more important process real solvents are used, it was necessary to decrease their undesired dissolving capacity by various measures e.g. by employing solvents already containing important quantities of solved substance among them also the artificial resin starting material, or by employing the solvent in the form of gas or vapor in order to avoid a too strong swelling of the grains of the artificial resin. Also solvents were recommended which have a dissolving power on the surface of the grains only at the temperature of their boiling point.

Now it has been found that grains of polyvinyl chloride can be combined excellently—whereby even preferably higher binding temperatures can be applied without danger for the porosity—if there are not employed solvents or swelling agents in order to facilitate a strong binding but real softening agents which before have been mixed with the thermoplastic material.

Surprisingly, the use of softeners, facilitating the sintering, is not only possible but even large amounts of softeners which can be more than 100 per cent, calculated upon the polyvinyl chloride, can be employed. This is extraordinary surprising because one had to expect a non-porous or at least an imperfectly porous substance if larger amounts of softeners are employed. The softeners do not only facilitate the sintering process but it is also most important that by this way softener-containing porous substances of desired softness and flexibility can be obtained, containing the softener in finest dispersion. This fact is very much important for many uses.

In practising this invention, the powdery or grainy substances are treated in a mixing apparatus with softeners or a mixture of softeners and volatile solvents which do not solve the polyvinyl chloride or solve it only in a little degree at temperatures under the sintering temperature, till the little parts of the powder resp. of the grains have absorbed the added softeners or the mixture of softeners and solvents completely or at least for the most part; then this composition is sintered at a suitable high temperature. The sintering is modified in a remarkable manner by the applying of softeners or mixtures of softeners and solvents. It may also be advantageous to employ mixtures of certain softeners and volatile solvents.

If the sintering is carried out on a free e.g. plain support or in a form which allows evading, the powdery resp. grainy substances rise and take up a larger volume. Hereby specially light and loose porous masses are obtained. They facilitate for instance the tearing into flocks for the filling of isolating rooms.

Generally one will work against such an expansion and loosening of the structure. This can be done for instance during the production of porous foils and plates by such a way, that the powder and the like containing softeners is not freely arranged in layers on the support but by putting a framing on the support which is completely filled up by the powder and by laying a cover on the framing. This prevents the rising of the mass if it is heated. On the other hand the inclination of the mass to rise gives a sufficient pressure against the cover to form a porous plate. It is useful to form the covering surface and likewise the support as a heating surface. In order to produce complicated porous molded articles corresponding molds are used which are covered at the filling opening and, if necessary, can also be heated at the side walls.

A specially solid structure and a desired small degree of porosity, especially a mikroporous structure is obtained by pressing the mass during the sintering by means of a suitably heated stamp or the like during the heating.

Other modifying measures consist in carrying out the sintering in a closed mold and causing in it an overpressure with the aid of a gas during the heating or an underpressure by vacuum. These measures are the more effective the more vacuoles are formed beside the open pores which depends as well on the kind of the employed polyvinyl chloride, on the addition of softeners or mixtures of softeners and solvents, and the

conditions of the heating (temperature and duration) and the pressure as executed by a stamp or by a preceding stamping.

In certain cases it may also be advantageous to carry out the sintering in an indifferent or chemical active atmosphere, for instance in an oxidizing, reducing, vulcanizing or chlorinating atmosphere.

Generally the sintering takes place the easier the more softeners or mixtures of softeners and solvents are contained in the powder and the like.

By the fact that the sintering proceeds the more rapidly and completely the more softener or mixtures of softeners and solvents are contained in the powder, the possibility is given to obtain molded articles which are partly porous, partly tight. E. g. such a plate is produced if a bottom layer consisting of a powder with many softeners is filled in a frame, a powder of essentially less softeners is piled on it and the heat treatment is so regulated that the upper layer becomes porous, the under layer melts together tightly.

The sintering according to this invention proceeds surprisingly so easily that it may also be carried out in situ on any surface which is to provide with a porous covering of polyvinyl chloride. For this purpose the polyvinyl chloride is brought in a brushable state. It is worked up with an adequate excess of a softener or a mixture of softeners and solvents. These agents must be of such a kind as to solve the polyvinyl chloride only slightly at temperatures under the sintering point. The polyvinyl chloride may also be worked up with a liquid which does not promote the sintering and does not solve, such as water or benzine, or with a binding agent, such as an adhesive solution with a volatile solvent or with a mixture of additions which cause the brushability. The thus obtained mass is brushed or smoothed on the surface to be covered, the volatile constituents are allowed to evaporate more or less; then the so obtained covering which can be suitably thickened by repeated charging is treated in situ by an instrument brought up to a suitable temperature, e. g. an iron, or a heated spatula or the like, under a suitable pressure till it is in the desired porous state.

If necessary, the added softeners or solvents or other liquids and binding agents may be partly extracted in the above described manner and thereby the obtained porous coverings can be hardened.

The selection of the softeners and solvents suitable for the sintering depends on the specific properties of the polyvinyl chloride which is to be worked up into porous masses. The selection can be made by a few simple solubility determinations at the temperature of the sintering point and under it, primarily at room temperature and, if necessary, at still lower temperatures. Generally the number of the suitable agents is the larger the higher molecular the polyvinyl chloride is. E. g. for especially high molecular polyvinyl chloride as it can be obtained for instance according to the French Patent 837,233, all usual softeners also in a mixture with nearly all volatile solvents are suitable with exception of the ketones, the aromatic chlorine hydrocarbons such as chlorotoluene and a few special solvents such as tetrahydrofurane.

To the powders containing softeners additions may also be incorporated—preferably solved in the sintering liquids—which influence the prop-

erties of the artificial material during or after the sintering. For this purpose stabilizers come into consideration such as lead salts, especially lead stearate or kaoline, also additions which cause a cross-binding action upon the molecules such as vinyl crotonate according to the German Patent Application W 106,747.

If the porous mass is to be brought in a flocky state the incorporation of gas-generating substances, such as ammonium bicarbonate, to the powder which is to be sintered may be advantageous. For this purpose the gas producing substances are preferably not incorporated in solutions but they are added to the powder of polyvinyl chloride in a solid state and in a relatively coarse distribution in order to obtain flocks of the desired size by the separating effect of the gas-generating substances.

In most cases the mixing of the powder of polyvinyl chloride and softeners or mixtures of softeners and solvents need not be carried out at a low temperature if the selection among them has been made usefully; the absorption can be accelerated by heating in most cases. E. g. a high molecular polyvinyl chloride with an equal part of weight of trikresyl-phosphate can be mixed with the methylglycol phthalate obtainable under the trade mark "Palatinol O", dibutyl phthalate ("Palatinol C") and the like, at about 70-100° without destroying the powder form. In the particular case the upper temperature limit for the mixing depends on the mutual relations of solubility, if volatile solvents are employed it depends naturally also on their boiling point.

Suitable sintering temperatures for powder of equal parts of high molecular polyvinyl chloride and softeners lie for instance at about 175° if methylglycol phthalate is used as softener, at about 150° if dibutyl phthalate is used, at about 130-140° if dihydro-isophorolacetate is applied. Usually the sintering temperature can be more lowered by additions of volatile solvents than by a sole incorporation of non-volatile softeners.

Suitable heating durabilities for the mentioned mixtures lie at about 30 minutes, if mikroporous plates of 10 mm thickness are to be produced, at about 15 minutes for plates of a thickness of 5 mm, and at about 10 minutes for plates of a thickness of 3 mm. The heating can importantly be shortened by preheating the powders to be sintered. That is specially to recommend if thicker articles are to be produced.

The size of the pores which are formed by the sintering can be influenced by a suitable selection of the size of the grains of the polyvinyl chloride, by the amount of softeners or mixtures of softeners and solvents, by the compression of the mass with the aid of a stamp and by the combination of these measures with corresponding sintering temperatures and heating durabilities, likewise also by applying under pressure or by increased gas pressure in the sintering mold.

If necessary, the produced mikroporous or coarse porous objects can be improved by a thermal after-treatment. Thereby temperatures are suitable which are close under the flowing point of the compositions. If volatile solvents are also employed in the production of the porous objects, the removal of them is usefully combined with the thermal improvement, carrying it out in a vacuum or in a current of gas.

If more softeners are employed for the facilitating of the sintering process than provided for the properties of the end products they can partly

be removed by subsequent extraction. A subsequent, if necessary partly exchange of the original softeners for new ones is also possible.

Example 1

200 parts of weight of a powder of high polymeric polyvinyl chloride which was sifted through a 200 mesh sieve were mixed with 200 parts of weight of trikresylphosphate C II S at 100° in a mixing apparatus. The thus obtained mixture which had preserved its powdery state was filled in an iron frame which was put on a heating plate. The completely filled frame was then covered by an iron plate in order to prevent an escaping of the mass when it was heated. By heating up on 170° the powdery mass was sintered within 10 minutes and yielded a completely equal mikroporous flexible plate of a thickness of 5 mm, of excellent properties of resistance. A stream of air or liquid can be easily blown through the plate, therefore the plate can be used as a filter and the like.

Example 2

In the same way as in example 1 a powder of high polymeric polyvinyl chloride consisting of larger particles was worked up; the powder was here obtained by a 75 mesh sieve. A relatively coarse porous but likewise excellent solid filter plate was yielded.

Example 3

200 g of a coarse grainy mixed polymerisate of the composition of 80 per cent of vinyl chloride and 20 per cent of vinyl acetate were equally mixed with 80 g of trikresylphosphate C II S at room temperature and sintered at 80° under a slight pressure for ten minutes. A soft rubber-like, coarse porous plate was yielded.

The porous polyvinyl chloride compositions produced according to this invention have an excellent resistance to tearing which is superior to that of porous rubber articles. The known properties of compact polyvinyl chloride could not give any hint about this superiority. On the contrary a less strength must be expected by the fact that the pores are open. This can only be explained by the surprising fact that the sintering spots of the parts of the polyvinyl chloride are still stronger than the original mass.

The resistance to temperature of the porous polyvinyl chloride compositions is also excellent. E.g. tubes of compact polyvinyl chloride are extruded through a nozzle at a temperature of 150°. Soiled filters of porous polyvinyl chloride, however, can be boiled out in glycerin at a temperature of 210–220° whereby they keep their structure and properties. The articles are even stronger after the boiling process.

The following valuable properties are also surprising: plates and blocks of the porous polyvinyl chloride compositions can be splitted into foils of a thickness of a few tenths of millimeter by the known leather splitting machine on account of their surprising strength. On the other hand these blocks and plates can be divided into elastic splinters or a porous wool by countersinking, stamping, turning on a lathe, planting and the like resp. they may be worked up to flocks by tearing machines.

Further the ability to be welded is surprisingly so good that it will do to weld the molded articles which are to be combined only at their borders. Thereby it is possible to produce complicated

composed articles of polyvinyl chloride which are completely porous.

A further advantage of the porous polyvinyl chloride compositions lies in the fact that they are also obtainable as working pieces the particular layers of which have different degrees of porosity, resp. partly an important one, partly no porosity at all. It is possible to carry out the sintering in the outward zone till the pores are completely closed, in other zones, however, only so far as open pores are formed; this is done by piling up layers of powder which sinter differently and by the application of suitable temperatures and pressures. For instance filtering cloths may be produced which are tight at their edges resp. at the fixing spots the main planes of which, however, are porous.

A further property of the polyvinyl chloride is that it can be brought into a porous state in situ on surfaces to be coated. If a plane support is to be coated the powder must be only piled on it and be ironed or calendered by a heated spatula or an iron and the like at a suitable pressure. If vertical or complicatedly formed surfaces are to be coated the powder is mixed with more liquid than it can absorb, if necessary also by employing binding materials. Then the paste is spread or smoothed on the surface to be coated. Hereafter the desired porous form may be obtained by ironing and the like; if necessary the mass can be previously dried or thickened by repeated spreading.

The porous polyvinyl chloride compositions can also be dyed much more homogeneously than the other artificial materials, especially rubber articles. The superiority in this respect is very important for many applications.

Beside these mentioned advantages there exist also the known valuable properties of the polyvinyl chlorides, especially their high molecular form: they are high resistant to most of the organic liquids, to concentrated acids, hydrogen peroxide, persulphate, halogens, alcalies, and other strongly corroding agents, even at high temperatures. They have a high insulating power and they are unflammable and insensitive against the action of the sun, the air, moisture and aging.

By the combination of the new and known properties many new kinds of applications have become possible. This combination makes the polyvinyl chloride superior to all other porous masses known till now; this superiority refers especially to the compositions with high and highest molecular polyvinyl chlorides. It occurs in all the applications of known porous masses. Further all those applications are possible in which the known porous masses could not be applied till now.

First the porous polyvinyl chloride compositions resp. the articles, flocks, splinters, wools and the like formed of them enlarge and improve the technical possibilities of the thermal, electric, and acoustic insulation in the arts, for building purposes, in the household, and for clothing purposes. The high resistance to temperature in connection with the extraordinary chemical strength and the excellent mechanic properties make them ideal insulating materials, specially for the purposes of the chemical industry. Since they can be produced with extraordinary fine porosity they are of a high value for heat insulations because they prevent any convection currents in the pores. The open pores of these porous articles do not hinder their application for cold insulat-

ing purposes because the open pores of the surface of foils and plates of polyvinyl chloride can be closed, as above described, so that no moisture can enter the inside pores and a formation of ice is not possible. Thereby the above described possibility to produce porous coatings in situ is also of a high value in many cases. If necessary, the outward openings of the pores may be closed by a suitable thermal after-treatment, for instance by fanning with a flame. On the other hand the division of the produced porous masses into flocks and elastic splinters and into insulating wools, as above described, which do not set after being slightly pressed on even if they are shaken for a long time, is often of a high importance for the filling of insulating hollow spaces.

The new porous compositions are also important for building purposes e.g. for the heat insulation of floors, walls, and ceilings, especially if they have surfaces with closed pores. The possibility to produce the coatings of floors, walls, and ceilings in situ, e.g. on plaster floors, is especially advantageous. Besides the open-porous coverings of polyvinyl chloride are also an excellent covering for moist walls or floors, if necessary for a support of tapestries, of coverings of linoleum and the like. Hereby, the ability of the porous polyvinyl chloride compositions to act sound insulating is very advantageous. Even foils of porous polyvinyl chloride can be obtained for floor coverings which have the effect of thick carpets on account of their excellent elasticity. The fact that polyvinyl chlorides can be dyed with much more different color tones than porous articles of rubber, and the like, and that it is odorless is specially important for these purposes.

All these advantageous properties can also be used for household articles, e.g. for stands, floor mats, rugs for bath-rooms, pads, and the like.

The new porous polyvinyl chloride compositions can also be applied for clothing purposes. The cleavability into thin foils makes it possible to produce feltlike resp. skin-like linings of suitable graduated porosity and flexibility and of a high heat insulating power. They can be applied as a substitute for the linings of fur but also for clothes e.g. for warming caps, gloves, jackets, and the like. If necessary, they may be made water-proof, resp. waterrepelling by sucking through solutions of waterrepelling substances, e.g. benzine, whereby their porosity is preserved. So it is possible to produce warming, light water-proof cloaks, caps, and the like, letting through the transpiration which have also a high resistance to nearly all corroding agents and are extraordinary good washable.

The application of all these advantages for the electric insulation is obvious. The possibility to produce porous coatings of polyvinyl chloride in situ is also hereby of high importance. E.g. windings of transformers can advantageously be coated in situ by such porous coverings in which insulating oil is then sucked in.

The new porous or mikroporous polyvinyl chloride compositions are also excellently suitable for the production of filters, e.g. dust filters, especially for the filtration of acid, chlorinating or oxidizing gases, for filter presses for large or small apparatus, for the filtration of drinking water, and the like, filter candles, diaphragms, e.g. for accumulators, electrolytic or osmotic cells, and the like. Their chemical and mechanical prop-

erties of resistance in connection with the above described advantages not known till now make them superior to all porous organic industrial material such as caoutchouc and the like which hitherto had been applied for such purposes. E.g. there are many more possibilities of cleaning soiled filters and the like: the filters of polyvinyl chloride may be boiled out in solvents such as glycerin at temperatures up to 210-220°. In most cases it is still more suitable to boil them out with constantly boiling hydrochloric acid of 20%. Surprisingly the strength of the filters is still more increased by the boiling. While the filters, diaphragms, and the like are insensitive to nearly all strongly corroding agents and to nearly all solvents, the porous polyvinyl chloride compositions can be removed if necessary from spots in apparatus which are hardly approachable: by the treatment with ketones, such as acetone, they decompose into powder.

For the manufacture of footwear the foils of polyvinyl chloride will have a great importance which is completely different from that of the artificial leather and of rubber hitherto applied. In contrast to these masses the artificial leathers of porous polyvinyl chloride let the transpiration pass through and are much more similar to the real leather because they are able to take up some moisture and can easily give it off. These advantages and the resistance to aging and the strength make the foils, furs, and skins of porous polyvinyl chloride superior to all other masses, if leather, especially deerskin is to be substituted by an artificial material.

Saddles, especially those for bicycles, may be produced of the porous and elastic polyvinyl chloride compositions. E.g. foils of porous polyvinyl chlorides are also very much suitable for elastic supports of tents protecting against moisture and the cold of the soil. Especially foils containing trikresylphosphate as softeners have only a slight permeability for water in spite of their porosity. They can be made completely impermeable for water if benzine containing oil is pressed or sucked through them. Stuffed goods, coverings for chairs, sofas and furniture, and the like can advantageously be produced of the new artificial materials. Especially flocks, splinters and wools of porous polyvinyl chlorides are an excellent material for stuffed goods which does not age. All these advantages can also usefully be applied for the production of gallantry articles such as hand-pockets, writing-supports, and the like.

It may still be mentioned that also leather grains or another plastic design may be obtained if porous foils are produced by sintering between two heating plates which are suitably equipped. Occasionally the possibility to spread the porous coverings in situ can also be important for the production of saddlers', harness-makers', and pouch and purse makers' wares.

The porous foils of polyvinyl chloride present new and progressive printing cloths and coatings for printing rollers. Beside their favorable mechanic properties, their stability and the possibility to be cleaned easily and thoroughly they are also able to take up the printing colors very well on account of their absorbing properties, and are thus an excellent reserve of colors.

On account of their suitability for strongly absorbed impregnations and the possibility that they can be brought on in situ, coatings of porous polyvinyl chloride are also very suitable for the protection of ship walls against sea animals and sea plants. The porous structure causes that the

animals and plants are poisoned much more effectively when they enter the pores containing poison than by the hitherto applied not porous poison paintings which lose their content of poison at the surface relatively quickly. In spite of their porosity the coatings of polyvinyl chloride compositions can be obtained with an outward smoothness sufficient also for these purposes.

The possibility to impregnate foils or coatings of porous polyvinyl chloride with strongly adhering poisons and if necessary to impregnate them with glue or other solutions of adhesive substance makes it also suitable for means for the extermination of animals and plants e.g. bandages for trees.

By its resistance to putrefaction and aging in connection with the well insulating properties the porous flocks, splinters, and wools can also be applied for the agricultural covering of the soil.

By all of the described properties, especially because it easily and thoroughly can be sterilized and cleaned, the porous polyvinyl chlorides are predestined for hygienic, orthopedic, therapeutic, and other medical applications.

Coarse porous molded articles of polyvinyl chloride can excellently be applied for bath sponges, rubbing gloves, and the like, thin split-foils can be used for the production of mouth-pieces for cigarettes, nikotine preserver for pipes, smoke consumers, foils which have to absorb perspiration, absorbing instep-raiser for shoes, protecting stockings which do not hinder the transpiration, for people with varicose veins, and other transmitting bandages. The foils which are porous on the upper side and unporous on the under side are especially suited for baby supports which can well be boiled out and sterilized.

For orthopedic applications the suitable regulation of the elasticity and porosity is highly im-

portant. Orthopedic instep-raisers, linings for corsets and in protheses, pressure balls for trusses and the like can better be produced of the new artificial materials and with a better suitability to the enquirements of every particular case.

For therapeutic applications the porous polyvinyl chlorides present important advantages by their compatibility with the various disinfectants and medicaments and by their excellent capability of absorbing if they are sufficient mikroporous. They can be applied as active fillers in poultices under stiffening bandages, pessaries, tampones, and the like. Their properties allow to apply them as medical deposits introduced into the tissue or in wounds or cavities of the body. Thereby it is also important that they can be brought in an absolute sterile state by simplest means. Foils produced with trikresylphosphate as softeners and fillers of mikroporous polyvinyl chloride have a permanent antiseptic effect by themselves.

The new products of porous polyvinyl chloride can also be applied for other medical and especially for surgical purposes. The application for sick-supports, especially for operation-supports which are absorbing on the upper side and impermeable on the under side and which can easily be sterilized after being used, is obvious. On account of their absolute indifference to all liquids of the body in connection with their absolute sterilizability and their capability of absorbing therapeutic active substances of every kind they may be applied instead of the hitherto applied medical deposits and plastic fillings to be laid in.

Their capability of absorbing which may still be more increased by suitable impregnations makes foils of mikroporous polyvinyl chlorides also a suitable artificial material for gas masks.

HERBERT BERG.
MARTIN DORIAT.

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF ADIPIC ACID

Wilhelm Nikolaus Mathes and Ludwig Seelmann,
Ludwigshafen/Rhein, Germany; vested in the
Alien Property Custodian

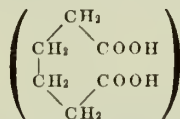
No Drawing. Application filed January 31, 1942

It is known to produce adipic acid from cyclohexane by boiling it with nitric acid. Furthermore adipic acid has been produced by the oxidation of cyclohexanol by means of nitric acid. Finally processes have been described which obtain adipic acid mixed with other products viz. in small quantities by submitting cyclohexen to strong oxidation conditions.

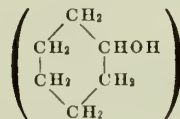
According to the present invention it has now been found that cyclohexen may be easily oxidized to adipic acid under ordinary conditions of oxidation, i. e. using nitric acid of preferably about 40-75% by weight. If simultaneously air is introduced into the reaction mixture it is possible to work with the theoretical amount of nitric acid or with a small excess. Of course it is also possible to use an excess up to about e. g. five times of the theoretical amount. Furthermore it is advisable to use catalysts favourable to oxidation, for instance oxides of manganese, iron, chrome or vanadium. Thereby the yields are improved.

The time of reaction depends on the temperature. The better the temperature of reaction will be kept constant by cooling the faster the cyclohexen may be added. Preferably the time of reaction takes about 1-2 hours and the reaction temperature may vary between 20° C and the boiling temperature of the nitric acid used. It is possible to apply pressure but thereby no important advantage is obtained.

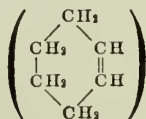
The process mentioned above in the first place (oxidation of cyclohexene) has never been used on a large scale. Compared with the known oxidation of cyclohexanol by means of nitric acid it is surprising that the new process works at least as satisfactorily to obtain adipic acid



as the known one, because cyclohexanol



already contains oxygen and it should be thought that it is more easily to oxidize cyclohexanol than cyclohexen



which does not contain oxygen. Furthermore cyclohexanol is soluble in watery nitric acid but not cyclohexen. Also this circumstance seems to

show that the known oxidation should be more easily carried out than the oxidation according to the invention.

When finally comparing the known process of treating cyclohexen under strong conditions of oxidation it is surprising that cyclohexen may be transformed to adipic acid under normal conditions of oxidation whilst in the case of strong conditions of oxidation only small amounts of adipic acid are obtained.

Example 1

A mixture of 90 g HNO₃ (80%) and 30 g H₂O are boiled under reflux and 20 g cyclohexen are added during 30 minutes. After further 30 minutes distillation by means of steam is carried out in order to remove small amounts of a contamination; finally 17,5 g raw adipic acid is obtained by evaporation.

Example 2

A round-bottomed flask provided with means for agitating, reflux-cooler and dropping funnel is filled with 425 g nitric acid of 50% and 0,3 g pentoxide of vanadium; 45 g cyclohexen are added under agitation during one hour, keeping the temperature of the acid to 55° C. In order to start the reaction it is advisable to heat at the beginning for a short time up to 70° C. If all of the cyclohexen has been filled in the temperature is raised to 100° C and maintained for an hour. After evaporation a paste of crystals is obtained consisting of 49,3 g raw adipic acid and small amounts of other acids.

Example 3

The device described in example 2 is furthermore provided with an inlet pipe for air. The conditions of reaction are the same and only the amount of nitric acid is reduced to 212,5 g; furthermore air is led in a moderate manner through the reaction mixture. Yield: 47,8 g raw adipic acid.

Example 4

In the device according to example 2 335 g of nitric acid of 65% and 0,3 g of pentoxide of vanadium are filled in. Thereto at first some drops of cyclohexen are added at 45° C and then during two hours at 30-35° C the rest of 47 g cyclohexen. The reaction mixture is kept to 40° C and then treated as described above. Yield: 56,5 g raw adipic acid.

Example 5

Instead of the pentoxide of vanadium according to example 2 0,5 g hydrate of the oxide of manganese are used. 47,4 g raw adipic acid are obtained.

WILHELM NIKOLAUS MATHES.
LUDWIG SEELMANN.

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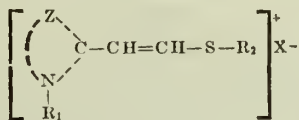
PRODUCTION OF NITROGENOUS HETERO-CYCLIC COMPOUNDS

Karl Kumetat, Wolfen (Kreis Bitterfeld), and
Oskar Riester, Dessau-Haideburg, Germany;
vested in the Alien Property Custodian

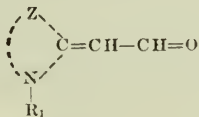
No Drawing. Application filed February 17, 1942

Our present invention relates to nitrogenous heterocyclic compounds and more particularly to the production of intermediate products for the preparation of dyestuffs especially cyanine dyestuffs.

We have found that salts of nitrogenous heterocyclic compounds which carry an ω -alkylmercaptoethene group in the α - or γ -position and have the following general formula:



wherein Z stands for a group of molecules necessary to complete a 5- or 6-membered ring usual in cyanine dye art as, for instance, indoline, oxazole, thiazole, selenazole, oxazoline, thiazoline, selenazoline, pyridine, lepidine, imidazole, quinoline or thiodiazole; these heterocyclic radicals may carry substituents such as alkyl, aryl, benzyl, phenylene, naphthylene and substituted phenyls or heterocyclic radicals or may be condensed with aromatic or heterocyclic rings, R_1, R_2 stand for alkyl or aralkyl and X stands for an anionic acid radical as, for instance, $\text{Cl}, \text{Br}, \text{I}, \text{ClO}_4, \text{SO}_4, \text{SO}_3\text{CH}_3, \text{SO}_3\text{C}_2\text{H}_5, \text{SO}_3\text{C}_6\text{H}_4\text{CH}_3$, are obtained by reacting heterocyclic 2 (or 4) -methene- ω -aldehydes of the formula:



wherein Z and R_1 mean the same radicals as mentioned above, in a solvent with phosphorus pentasulfide and treating the thus resulting thioaldehyde with alkylhalides or reactive alkyl esters. The heterocyclic 2-methene- ω -aldehyde may be prepared by the process disclosed in U. S. application Ser. No. 176,063 filed November 23, 1937. In the treatment with phosphorus pentasulfide aromatic hydrocarbons in which the ω -aldehydes are soluble as, for instance, benzene, toluene, or xylene may be used as solvents. The phosphorus pentasulfide is used in such an amount that at least 1 mol thereof is applied to 1 mol of aldehyde. The thioaldehyde is obtained by concentrating the reaction liquid or precipitating, for instance, with benzene of methylisoheptane. The thioaldehyde is condensed with alkylhalides or reactive alkyl esters. This reaction may be accomplished by reacting the alkylating agents or the thioaldehyde, if neces-

sary in the presence of a solvent as, for instance, methanol or benzene. As alkylating agents alkylbromide, alkyl iodide, alkylsulfate or alkyltoluene-sulfonate are, for instance, suited.

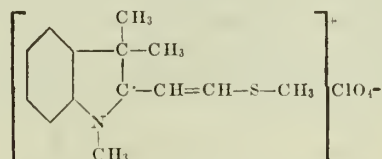
5 The compounds prepared by the process of the present invention are valuable intermediate products in the preparation of dyestuffs especially cyanine dyestuffs. They readily react with active methylene or methyl groups with the formation of merocyanines or polymethine dyestuffs. The dyestuffs derived from these intermediate products are obtained in a purer form and with a better yield than they are by processes hitherto known. Owing to the reactivity of the intermediate product it is also possible to cause such compounds containing methylene or methyl groups to react as have not hitherto been capable of forming dyestuffs.

The more detailed practice of the invention is illustrated by the following Examples. There are, of course, many forms of the invention other than these specific embodiments.

Example 1

25 300 g of 1.1.3-trimethylindoline-2-methene- ω -aldehyde are dissolved in 2 liters of benzene. To the mixture 450 g of phosphorus pentasulfide are added. The whole is boiled for two hours and filtered. The filtrate is clarified with charcoal, concentrated and precipitated with benzene. Melting point $110-111^\circ \text{C}$.

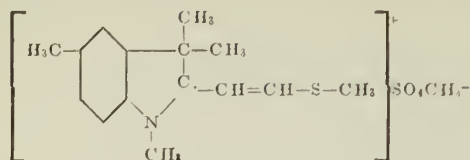
21 g of the thioaldehyde thus prepared are dissolved in 100 cc of methanol and mixed with 30 cc of dimethylsulfate at 50°C . After cooling 100 cc of an aqueous sodiumperchlorate solution of 20% strength is added thereto. 28 g of a compound of the following formula with a melting point of 225°C crystallize out:



Example 2

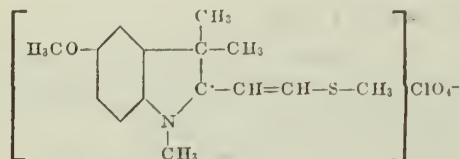
1.1.3.6-tetramethylindoline-2-methene- ω -aldehyde is reacted with phosphorus pentasulfide in the manner as described in Example 1. If the thioaldehyde thus obtained and having a melting point of $199-201^\circ \text{C}$ with decomposition is treated with dimethylsulfate, a reaction product having

a melting point of 191° C and the following formula is produced.



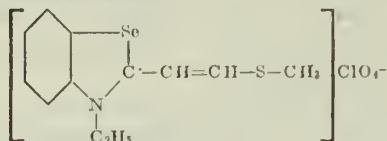
Example 3

1.1.3-trimethyl-6-methoxyindoline-2-methene- ω -aldehyde is treated in the manner as described in Example 1. The thioaldehyde obtained melts at 170–172° C. The dimethyl sulfate addition product is treated in the manner as described in Example 1. It then melts at 225° C with decomposition and has the following constitution:



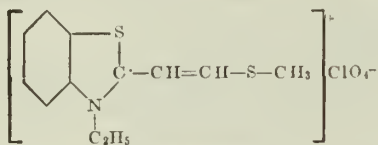
Example 4

3-methyl-benz-selenazoline-2-methene- ω -aldehyde is reacted with phosphorous pentasulfide in the manner as described in Example 1. The oily reaction product is treated with dimethylsulfate and precipitated with sodium perchlorate. The resulting product melts at 200° C and has the following constitution:



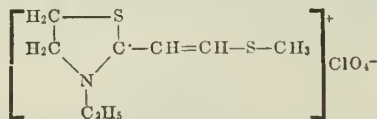
Example 5

3-ethyl-benzthiazoline-2-methene- ω -aldehyde is transformed into the thioaldehyde in the manner as described in Example 1. The reaction product is treated with dimethylsulfate and precipitated with sodium perchlorate. The resulting product melts at 178° C and has the following formula:



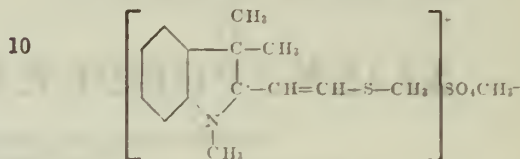
Example 6

3-ethyl-thiazolidine-2-methene- ω -aldehyde is treated with phosphorus pentasulfide in the manner as described in Example 1. The oily reaction product thus obtained is condensed with dimethylsulfate. On precipitating with sodium perchlorate a compound having a melting point of 99° C and the following formula is produced.



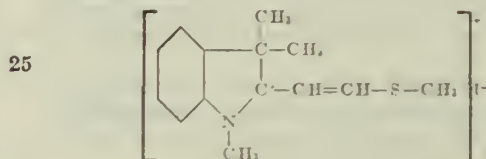
Example 7

1/10 mol of the thioaldehyde obtained in the manner as described in Example 1 is dissolved in 150 cc benzene and mixed with 1/10 mol of dimethylsulfate. After some time an addition compound having a decomposition point of 143–145° C and the following formula crystallizes out.



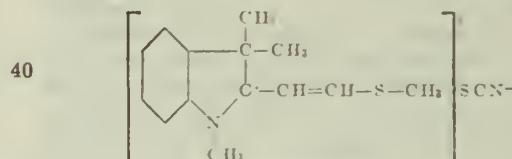
Example 8

The addition compound of Example 7 is dissolved in water and mixed with an excess of an aqueous potassium iodide solution of 20% strength. A compound having a decomposition point of 226–227° and the following constitution crystallizes out:



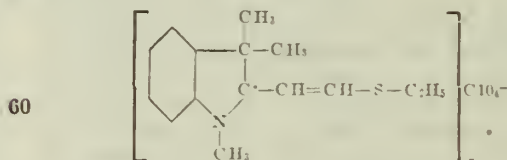
Example 9

The addition compound of Example 7 is dissolved in water and mixed with an aqueous ammonium thiocyanate solution of 20% strength. A compound with a decomposition point of 193–196° C and having the following formula crystallizes out:



Example 10

1.1.3-trimethylindoline-2-methene- ω -aldehyde is transformed into a thioaldehyde in the manner as described in Example 1. 21 g of the thioaldehyde are dissolved in 80 cc of methanol heated to 50° C. 35 cc of diethylsulfate are then added to the solution whereupon the mixture is kept at 50° C for 5 minutes. After cooling to 0° C 100 cc of a sodium perchlorate solution of 20% strength is added thereto. A compound of the following constitution crystallizes out:



KARL KUMETAT.
OSKAR RIESTER.

ALIEN PROPERTY CUSTODIAN

VARNISH WITH A BASE OF FORMO-PHENOLIC RESIN RENDERED SUPPLE AND METHOD FOR OBTAINING THE SAME

Louis René Joseph Kientz, Paris, France; vested in the Alien Property Custodian

No Drawing. Application filed February 26, 1942

The object of the present invention is to prepare a varnish, with a base of formo-phenolic resin, possessing in particular remarkable properties of suppleness, adhesion and stability with respect to chemical and physical agents. In particular, this varnish allows to obtain, by application thereof onto an underlying base, a film which is capable of lending itself without scaling to deformations produced by shocks or by temperature variations, while presenting a great hardness. Such properties allow to utilize the varnish obtained according to the invention as both an effective and lasting coating or facing to protect metallic or other objects against the destructive or corrosive action of the atmospheric or chemical agents to which they are exposed.

The invention relates more particularly to a method for preparing the above defined varnish. This method essentially consists in preparing a formo-phenolic resin by condensation of a phenol with formaldehyde in an alkaline medium and in the presence of a catalyser constituted by the salt of an organic acid having at least one hydroxylic function, then in mixing the resin thus obtained, preferably in the presence of organic solvents, with a resinous product resulting from the acid treatment of aromatic hydrocarbides having a high molecular weight and presenting very developed lateral chains.

A mixture is thus obtained which, after having been possibly diluted by means of organic solvents appropriate for the utilization of the considered varnish, becomes, by a subsequent condensation, a plastic mass having the above mentioned properties.

In practice, this condensation will take place on the very object which is to be coated after the mixture has been applied onto the object.

Except for the presence of the salt of an organic acid acting as a catalyser, which condition constitutes one of the characteristics of the invention, the preparation of the formo-phenolic resin in an alkaline medium may be effected by the usual methods. The alkaline medium will preferably be constituted by a volatile alkali, such as ammonia for example, or by an organic amine such as diamine-ethylene.

The salts of the organic acids having at least one hydroxylic function which may be utilized as catalysts in this reaction are particularly the salts of citric, tartaric, malonic and lactic acids.

As examples of aromatic hydrocarbons having a high molecular weight and a developed lateral chain, the resinous derivatives of which may be utilized for being mixed with the formo-phenolic

resin, cumarone (C_9H_6O) and indene (C_9H_8) which are to be found in the distillation products of coal and of petroleum may be utilized. It is known that, as a result of an acid treatment, these substances yield resinous products the constitution of which is not very well defined, but which are characterized in particular by their resistance to acids and to alkalis. Such products are now well known in industry and their preparation does not need to be specially described.

Before they are mixed, the formo-phenolic resin and the resin of the aromatic hydrocarbide may be dissolved, respectively, in solvents suitable for each one of them, it being necessary to choose the solvents in such a way that they be miscible one with the other. As solvents for the formo-phenolic resin, ethyl alcohol, acetone, or a mixture of one of these with butanol may be used for example. As a solvent for the resin of the aromatic hydrocarbide, an aromatic hydrocarbide such as benzene may be utilized.

It should be noted that, in all cases, the mixture of the two above defined resins is not soluble in vegetable and mineral oils neither in the presence of cold or of heat.

It has been discovered, according to the invention, that the condensation of both resins can be effected only if these products are mixed in proportions comprised within well determined limits. The proportion of formo-phenolic resin entering into the composition of the mixture must lie between 75 and 50% by weight, and the proportion of the resinous product derived from the aromatic hydrocarbide between 25 and 50%.

As has been said above the condensation of the two resinous products thus mixed is effected on the underlying base object coated or veneered with this mixture. This reaction takes place as a result of a heating operation at a temperature which may vary from 180 to 450° C, which baking operation is prolonged for a period of time which may vary, dependent upon the thickness of the coating, the size of the coated object and the temperature chosen, from a few minutes to 2 hours.

The coating obtained after this treatment is insoluble in the usual organic solvents.

As has been mentioned above those properties of suppleness, adherence and physical and chemical stability of the varnish according to the invention render it particularly suitable for use as a coating or facing for protecting metallic or other objects against the destructive or corrosive action of atmospheric or chemical agents to which they are exposed.

Thus, for example, this varnish may be advantageously utilized to replace, in a large number of cases, methods for protecting iron or other metals by tin-plating, galvanizing or other metal-lising processes. Among other applications of this kind, it may be used in the constitution of protective coatings for the inner and outer surfaces of tin cans for canned food or of metallic containers the object of which is to contain chemical products; for parts exposed to the inclemency of the weather and accessible only with difficulty,—thereby requiring a resisting coating, capable of long wear, which condition is habitually obtained by galvanising—, as is the case for example for certain parts of the supporting towers or framework of electric transmission feeders; for metallic parts or objects utilized in the spinning and dyeing industries which parts or objects are subjected to the action of chemical reagents.

The varnish according to the invention may also be utilized as a coating or facing product for objects made of magnesium or of magnesium alloys instead of having recourse to chemical mordanting, generally utilized for protecting these objects.

Here is a non limitative example of how the invention can be embodied:

On the one hand, 3 gr. of tartaric acid are dissolved in 7 gr. of water and the solution obtained is mixed with 50 gr. of ammonia at 20% and 200 gr. of formaldehyde at 40%.

5 On the other hand, 250 gr. of phenol are melted in a glass balloon shaped container and the above described preparation is added thereto. The whole is mixed and the balloon provided with an ascending refrigerator is placed in a bath of oil heated to 130–140° C.

10 The reaction starts off rather violently. The products of this reaction separate little by little into two layers. When this separation is completed the upper layer is decanted then the resin thus obtained is dehydrated under a vacuum and it is diluted in a mixture of 125 grs. of acetone and 125 grs. of butanol.

15 Finally, this resin solution is mixed with a solution of 90 grs. of coumarone resin (fusion point 80–81° C) in 250 grs. of pure benzene. A varnish is thus obtained which is ready for use. This varnish may be applied preferably by immersion or by spraying. The final condensation is effected by a baking operation under those conditions of temperature and of time already indicated.

25 LOUIS RENÉ JOSEPH KIENTZ.

ALIEN PROPERTY CUSTODIAN

PROCESSES FOR THE AMELIORATION OF RUBBER

Jean Nicolas Louis Le Bras and Patrice Henri Marie Compagnon, Paris, France; vested in the Alien Property Custodian

No Drawing. Application filed April 3, 1942

The present invention relates to processes for the amelioration of natural rubber. They essentially consist in causing a copolymerization of rubber and unsaturated bodies, more particularly polymerizable vinylic monomers, the vinyl remainder of which is attached to at least one atom, or group of atoms, having electro-negative features.

It is known that copolymerization consists in effecting polymerization on a mixture of monomers, the properties of said copolymers being often very different from that of the polymers of each of the monomers. Many examples of copolymerization are known and many products thus obtained have acquired industrial importance. For instance, can be cited the copolymers of vinyl chloride and vinyl acetate, acrylic acid and vinylic esters, acrylic acid and butadiene, and, in the particular field of synthetic rubber, the copolymers of butadiene and styrolene, of butadiene and acrylic nitrile, etc. It is moreover remarkable to find that in the copolymerization can be caused to intervene products which are not, in themselves, polymerizable: such is the case for instance, for maleic anhydride which forms copolymers with styrolene, vinyl chloride

It must be noted from now that, as regards rubber, the terms "polymerization" and "depolymerization" are most often used without keeping sufficiently to their strict chemical sense. Rubber being already a polymerized substance, mention can scarcely be made but of an increase of its degree of polymerization in the case of the union of its filiform molecules. On the other hand, depolymerization must designate, substantially, the return to the monomer, isoprene in this case, and not only a breaking up of the molecular chain into more or less long links; however, it can logically be said that depolymerization occurs when said breaking up takes place with formation of double bonds at the ends of the links.

As regards the term "copolymerization," it is used herein in the exact sense attributed to this word, that is to say that it is admitted that the rubber molecules are united together, either by chain, or by bridge, or by both these means, through the medium of molecules of the other monomer utilized. It will be easily understood that said polymerization can apply either to rubber hydrocarbon, or to unions of the molecules of said hydrocarbon, or finally to sections of said molecules.

It has already been proposed to introduce into

the latex, emulsions of polymerized vinylic derivatives, in order to obtain in the midst of the rubber, a perfect dispersion of said polymers and to eventually improve the properties of the mixture; but, in these prior methods, there is no chemical connection between the rubber and said polymers, and the improvement produced is relative and due to charge effect. The tests subsequently effected in order to obtain, in the very midst of the latex, the polymerization of the monomers have given no practical result, according to literature.

On the contrary, according to the present invention, copolymerization involves a profound modification of the properties of the product obtained, modification which is due to variations of the chemical structure and which, most often, results in nearly complete insolubility in the usual rubber solvents, of the coagulation product of the aqueous dispersions treated.

The principle of said invention is to cause rubber, from any botanical source, to react in an aqueous dispersion, in presence of a protecting colloid and of a suitable catalyser, with unsaturated derivatives such as those above mentioned.

As aqueous dispersions can be used natural latex, or any product of its coagulation, or of its evaporation, put again in suspension. In both cases, the rubber may have been previously subjected to a treatment for degrading it (malaxation, heating, oxidation, etc.), to peptization, or to a treatment for increasing its degree of polymerization.

As protecting colloid, use can be made of agents generally recommended for emulsifying and stabilizing latex in particular, for instance, oleates, stearates, various sulphonates, albuminoids.

The catalyser can be, for instance, a peroxide or a mixture of peroxides. Good results have been obtained with hydrogen peroxide, or organic peroxides usually used for polymerizations.

As example of copolymerizable monomers can be cited styrolene, acrylic acid, acrylic esters, acrylic nitrile, acrolein, separately or in mixtures.

The reaction also takes place, as in the general case of copolymerization, with products which are not polymerizable in themselves.

The monomer and the catalyser are added to the duly stabilized rubber dispersion; the whole is then stirred; the temperature and the time of contact depend on the degree of polymerization it is desired to obtain. After reaction, the dispersion is coagulated in the usual manner; it can also be evaporated.

The coagulation products differentiate, most

often, from ordinary latex coagulum, by a practically complete insolubility in rubber solvents (benzene, gasoline . . .) and a relatively limited swelling. They can however be malaxated and can be vulcanized according to the usual methods; according to the starting monomer and the conditions of polymerization, the vulcanized products obtained by means of the rubber thus modified can swell considerably less in the solvents than those obtained by the same rubber non-modified.

The examples previously cited and the experimental details hereinafter are given in order that the invention may be clearly understood, but must not be considered as limiting the same in any way whatever.

Example 1

Latex free from ammonia is brought to a 20% content in dry rubber. Thereto are added one or more emulsifying stabilizers, such as sulphonated fatty alcohol, soap, etc. (1 to 2 grs. for 100 cubic centimeters of diluted latex), and a protecting colloid (gelatin: 1%). Acrylic nitrile is added (50 parts for 100 parts of dry rubber) and then hydrogen peroxide so as to obtain 2 to 10 cubic centimeters of active oxygen per gram of dry rubber.

The mixture is carefully emulsified, then maintained at a temperature of 50 to 60° for 24 hours.

The reaction product, constituted by a homogeneous jelly, is treated with diluted acetic acid, then filtered and dried. An opaque and somewhat fibrous mass is obtained which gives, after passage through a mixer, a translucent crepe quite similar to ordinary crepe. It differentiates therefrom by certain of its properties, in particular its insolubility in ordinary rubber solvents.

This crepe can be mixed, charged and vulcanized in the usual manner.

The vulcanized product possesses a clearly improved resistance to swelling agents.

Example 2

The same operations are effected as in the preceding example with the only difference that hydrogen peroxide is replaced by ethyl hydroperoxide.

Example 3

The same operations are effected as in the preceding example, by replacing acrylic nitrile by styrolene.

Example 4

To the latex stabilized as previously stated are added ethyl hydroperoxide, styrolene (30 parts for 100 parts of dry rubber) and acrylic nitrile (30 parts).

Example 5

The same operations as in example 2 are effected, but by replacing acrylic nitrile by butyl methacrylate.

Example 6

The rubber contained in the latex is degraded by heating said latex with or without hydrogen peroxide, then treated as previously.

Example 7

The same operations are effected as in any one of the preceding examples by progressively adding the monomer or monomers and the catalyser, and stirring.

Example 8

Examples 1 and 2 are applied to an artificial latex prepared in the following manner:

Rubber is malaxated for $\frac{3}{4}$ of an hour in the cold state, then heated for an hour and a half at 250° in an inert gas; in these conditions, a viscous liquid mass is obtained having a non saturation only slightly lower than that of raw rubber.

This liquid rubber is placed in solution at 50% in benzene; the solution is emulsified in water containing a soap (oleate of Na: 1%), a dispersing agent (darvan: 1%), a protecting colloid (casein: 1%); after elimination of the benzene, the emulsion very rapidly gives a cream which contains about 50% of liquid rubber.

The copolymerization product obtained from said cream is a solid and plastic mass which can be worked and vulcanized as ordinary rubber.

In the preceding description, only reactions are mentioned concerning natural rubber or such rubber which has been subjected to treatments affecting the rubber-hydrocarbon, but, of course, the reaction can also be used for a natural rubber, which has been subjected to treatments affecting the components having not the character of rubber, for instance deproteination.

The description mentions as a catalyser for facilitating the reaction of the organic peroxydes, but this reaction can also be facilitated by means of all other physical or chemical agent promoter of polymerisation.

JEAN NICOLAS LOUIS LE BRAS.

PATRICE HENRI MARIE COMPAGNON.

ALIEN PROPERTY CUSTODIAN

PROCESSES FOR THE AMELIORATION OF RUBBER

Patrice Henri Marie Compagnon and Jean Nicolas
Louis Le Bras, Paris, France; vested in the Alien
Property Custodian

No Drawing. Application filed April 3, 1942

The present invention relates to processes for the amelioration of natural rubber. They consist in causing the rubber and unsaturated bodies, more particularly polymerizable vinylic monomers, the vinyl remainder of which is attached to at least one atom, or group of atoms, having electro-negative features, to chemically react, by treatment in a mixer.

In the patent of the same date, the inventors have described a method allowing to effect the copolymerization, in an aqueous dispersion, of rubber and of such derivatives. Now, they have found, according to the present invention, that a similar and probably identical reaction, was capable of taking place by simply mixing the constituents in a mixer having tightly clamped cylinders.

It must moreover be pointed out that, in the same way as unsaturated products non polymerizable in themselves can be caused to intervene in a copolymerization, such compounds can give rise to the reaction in a mixer. It is the case, in particular, for maleic anhydride, the use of which substance, by its very nature, could not be thought of when working in an aqueous dispersion.

However, the fact that such products can intervene for uniting together molecules, or sections of molecules of rubber, allows of including them in the description of this invention, under the designation of "monomers."

It will be easily understood that the very conditions of the operation, which lend themselves to the use of solid or liquid substances having a relatively high boiling point, render difficult the utilisation of substances having a relatively low boiling point and can then lead to a less extensive field of application than when working in an aqueous dispersion.

The principle of the invention is therefore to cause to react together, by a simple treatment in the mixer, the rubber, from any botanical source, and the previously mentioned unsaturated derivatives. For that purpose, the following method of procedure is adopted: after masticating the rubber, the cylinders are tightly clamped, then the derivative to be combined is incorporated with the liquid rubber, with or without a catalyser. The reaction which occurs, appears, when it has acquired a certain degree, by a "drying up" of the liquid rubber; if it is carried too far, the passage to a creped aspect and to a crumbling of the sheet can be noticed in certain cases.

According to the monomer utilised, the reac-

tion will be effected with or without a catalyser. As catalysers, use can be made, as for the copolymerization, of peroxides; benzoyl peroxide for instance is well adapted, owing to its physical state, to the conditions of operation utilised.

The fact that, in certain cases, catalysers can be dispensed with, allows it to be assumed that, according to the degree of reactivity of the monomer, the conditions of operation can be sufficient for causing the reaction: the latter would then be promoted, either by peroxides, the formation of which during the mixing of the rubber is well known, or by electric phenomena which arise during said mixing, or, again, by the pressure exerted on the mixture when it is rolled.

Besides the existence of catalysers, that of inhibitors is noticed; the latter are numerous and it is curious to find, among them, the presence of reducing agents such as hydroquinone, and of oxidizing agents, such as trinitro-benzene.

As example of monomers, can be cited, acrylic acid, acrylic nitrile, styrolene, maleic anhydride, separately or in mixtures.

The products obtained differentiate, most often, from ordinary rubber, by a practically complete insolubility in rubber solvents (benzene, gasoline, . . .) and a relatively limited swelling. Moreover, a slight thermoplasticity and nervousness of the reaction products is noticed which render the monomers used in these conditions first-class "stiffeners." The modification of the chemical structure is so preponderant that it suffices, for instance, to fix, by means of the mixer 1% of maleic anhydride for the rubber thus modified, although apparently similar to an ordinary masticated rubber, to become practically insoluble in benzene; on the contrary, the same natural rubber, mixed in the same conditions, but without addition of monomer, is completely and rapidly dissolved when in contact with benzene.

Rubbers thus modified can be more or less plastified according to the degree of polymerization, and can be vulcanized according to the usual methods; according to the starting monomer and the conditions of the reaction, the vulcanized products obtained can swell considerably less in the solvents than those obtained by the same rubber non modified.

Briefly, it is apparent from the preceding description that the reaction produced occurs between the same agents and gives the same modifications of the properties as that which has been indicated in the patent of the same inventors on copolymerization in an aqueous dispersion; it

must therefore be considered also as a copolymerization. It must be pointed out that, to their knowledge, this is the first example of copolymerization carried out in such conditions.

It will be easily understood that if, chemically, the same results can be obtained by treatment in a mixer or by reaction in an aqueous dispersion, the methods of application of the various monomers can be adjusted according to their state and physical properties.

It is also obvious that the same reaction can take place if the rubber has been previously subjected to a treatment which degrades it (malaxation, heating, oxidation, etc.), to a peptization or to an increase of its degree of polymerization.

The examples previously mentioned and the experimental details hereinafter are given in order that the invention may be clearly understood, but must not be considered as limiting the same in any way whatever.

Example 1.—To malaxated rubber is added 5% of maleic anhydride, between slightly spaced cylinders. The addition terminated, the mixture is malaxated between tightly clamped and cold cylinders. The reaction occurs more or less rapidly according to the quantity of rubber in course of treatment.

The reaction product differentiates from ordinary malaxated rubber by greater nervousness, slight thermoplasticity and nearly complete insolubility in the usual rubber solvents. It can be however treated in the mixer as easily as ordinary

rubber, it also lends itself to roving and calendering operations. It can be vulcanized by the usual processes. But, for obtaining good mechanical properties, the retarding effect of maleic anhydride must be corrected by the addition of neutralizing products, polyalcohols, amines, polyamines, etc.

The nervousness and slight thermoplasticity of the malaxated product renders maleic anhydride a "stiffening" agent superior to all those known up to now. It allows of vulcanizing, in live steam, sheets, threads, tubes, etc. non charged, without appreciable distortions being observed thereby.

The vulcanized mixtures offer good resistance to swelling agents.

Example 2.—To malaxated rubber is added 2% of benzoyl peroxide, then 10% of acrylic acid; the reaction is effected between tightly clamped and cold cylinders as in example 1.

Example 3.—The same operations as in example 2 are effected, acrylic acid being replaced by acrylic nitrile. Owing to the volatility of nitrile, a great part of said reagent is lost by evaporation.

Example 4.—To liquid rubber (obtained according to the method indicated in example 8 of the inventors' Patent of the same date) is added 2% of benzoyl peroxide and poured over the cylinders of a mixer; 15% of maleic anhydride is added, the reaction is effected as above stated and a solid sheet similar to the preceding ones is obtained.

PATRICE HENRI MARIE COMPAGNON.
JEAN NICOLAS LOUIS LE BRAS.

ALIEN PROPERTY CUSTODIAN

TERTIARY AMINES OF THE ACETYLENE SERIES AND A PROCESS OF PRODUCING SAME

Walter Reppe, Ernst Keyssner, and Otto Hecht,
Ludwigshafen-on-Rhine, Germany; vested in
the Alien Property Custodian

No Drawing. Application filed April 29, 1942

The present invention relates to tertiary amines of the acetylene series and a process of producing same. This application has been divided out from application Ser. No. 216,962, filed July 1, 1938.

We have found that amino compounds of the acetylene series, i. e. amines having a triple carbon linkage, can be obtained in a manner which is simple industrially by treating methylolamino compounds with acetylene in the presence of catalysts. Suitable methylol amino compounds are those obtainable by condensing aldehydes or ketones with amino compounds, e. g. methylol-isobutylamine, especially such methylol compounds as contain exclusively tertiary basic nitrogen atoms as are obtained by condensing aldehydes or ketones with secondary amines or heterocyclic secondary bases, for example with dimethylamine, diethylamine, dibutylamine, diisobutylamine, diethanol amine, N-alkylanilines, N-alkylnaphthylamines, dicyclohexylamine, piperidine or morpholine.

Suitable catalysts are the heavy metals of the first and second groups of the periodic system and their compounds, in particular copper and its salts, as for example copper chloride or cuprous chloride, copper acetate, copper formate or acetylene-copper compounds. It is often preferable to use either basic compounds, such as ammonia or amines or ammonium or amine salts, alkali or alkaline earth metal salts during the condensation or to carry out the process in a weakly acid medium. The process may be carried out in the presence or absence of solvents, as for example water or organic solvents miscible with water, such as alcohols, dioxane or low molecular fatty acids. The temperatures depend on the initial materials used; the condensation often takes place even at ordinary or slightly elevated temperature. Generally speaking, the temperatures necessary for the reaction do not exceed about 120° C. It may be carried out at atmospheric pressure, and also under increased pressure, for example at pressures between 2 and 40 atmospheres. Highly concentrated acetylene or acetylene diluted with any foreign gases may be used, as for example electric arc acetylene.

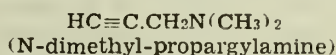
The condensation according to this invention proceeds with the splitting off of water and the adding on of the acetylene radicle to the carbon atom of the methylol compound. The condensation may take place with one or with both of the hydrogen atoms of the acetylene. The condensation products obtained are, by reason of their triple carbon linkage, especially reactive and may be subjected to polymerization, either directly or

after conversion of the triple linkage into a double linkage, resinous substances thus being obtained. They are also valuable initial materials for the preparation of solvents, pharmaceuticals and dyestuffs. For example, the acetylene derivatives still containing a hydrogen atom in the acetylene radicle yield with alcohols in the presence of strongly alkaline substances vinyl ethers which are readily convertible into carbonyl compounds by the splitting off of the alcohol radicle and rearrangement.

The following Examples will further illustrate how this invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight.

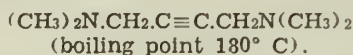
Example 1

822 parts of glacial acetic acid are added to 450 parts of 50 per cent aqueous dimethylamine while stirring and cooling between 10° and 20° C. The resulting solution is charged together with a solution of 40 parts of copper acetate in 972 parts of 40 per cent formaldehyde into a pressure-tight boiler. 5 atmospheres of nitrogen and 10 atmospheres of acetylene are pressed in consecutively and the whole is stirred at 40° C until no further decrease in pressure takes place. The acetylene used up is replenished by pressing in fresh acetylene from time to time. After from 10 to 20 hours, the absorption of acetylene is completed. For each molecular proportion of the dimethyl-methylol amine used, 1 molecular proportion (in all about 280 parts) of acetylene is absorbed. The reaction mixture is freed by filtration from the deposited acetylene-copper compound and there is added to the clear, pale red-brown filtrate an amount of 47.6 per cent caustic soda solution corresponding to the amount of glacial acetic acid used while stirring and cooling: two layers are thus formed. After separating the upper layer which consists of a concentrated, about 70 per cent, aqueous solution of the reaction product, the lower aqueous salt solution is exhaustively shaken with ether. The ether is evaporated from the extract and the residue combined with the separated upper layer. This product is dried with solid caustic potash and then subjected to fractionation. In addition to a small amount of first runnings and a residue, there is thus obtained a main fraction of an amine boiling between 79° and 80° C and having the constitution:



in a yield of about 70 per cent. There is also

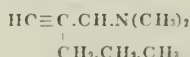
formed in a small amount (about 10 per cent) as a by-product, tetramethyldiamino-dimethylacetylene of the formula:



If a corresponding amount of isobutylamine be used as initial material instead of the dimethylamine, N-isobutyl-propargylamine having a boiling point of from 134° to 136° C is obtained in a good yield.

Example 2

567 parts of formic acid are added to 225 parts of 50 per cent aqueous dimethylamine while stirring and cooling at from 10° to 20° C. 360 parts of butyraldehyde and 10 parts of copper chloride are then added. The resulting solution is treated at 40° C with a mixture of acetylene and nitrogen in the manner described in Example 1. The absorption of acetylene is completed in about 8 hours. The reaction product is worked up as described in Example 1. The alpha-propyl-alpha-N-dimethyl-propargylamine of the formula:



thus formed in a good yield boils at from 134° to 136° C.

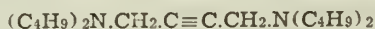
Small amounts of the corresponding dialkylated acetylene are formed as a by-product.

Example 3

252 parts of glacial acetic acid and 10 parts of cuprous chloride are added to 516 parts of di-butylamine while stirring and cooling at from 10° to 20° C. After adding 300 parts of 40 per cent formaldehyde, the mixture is treated at from 30° to 40° C in a pressure-tight vessel with a mixture of acetylene and nitrogen as described in Example 1. 1 molecular proportion of acetylene is absorbed for each molecular proportion of amine. The reaction product consisting of two layers is freed by filtration from acetylene copper compound and neutralized with caustic soda solution. The two layers are then separated from each other. The upper layer, consisting of almost pure propargyl-(di-normal-butyl)-amine of the formula:



is dried with solid potassium hydroxide and then fractionally distilled; there are obtained a yield of 80 per cent of propargyl-di-normal-butyl)-amine having a boiling point of from 87° to 89° C at 19 millimeters (mercury gauge) and a yield of about 10 per cent of tetra-normal-butyl-diamino-dimethyl-acetylene of the constitution:

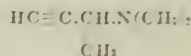


having a boiling point of from 133° to 135° C at 1 millimeter (mercury gauge).

Example 4

1370 parts of 98 per cent formic acid and 10 parts of cuprous chloride are added to 500 parts of 50 per cent aqueous dimethylamine while stirring and cooling. 225 parts of 98 per cent acetaldehyde are added to the resulting solution which is then treated in a stirring autoclave at from 25° to 30° C with a mixture of 10 atmospheres of acetylene and 5 atmospheres of nitrogen until no further absorption of acetylene takes place. By working up in the manner described in Example

1 there is obtained in a good yield alpha-methyl-N-dimethyl-propargylamine of the constitution:

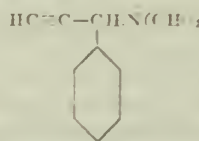


in addition to small amounts of the corresponding dialkylated acetylene.

Example 5

A solution prepared at from 10° to 20° C, of 225 parts of 100 per cent dimethylamine, 330 parts of glacial acetic acid and 10 parts of cuprous chloride has added to it 530 parts of benzaldehyde, the whole then being treated with a mixture of 5 atmospheres of nitrogen and 10 atmospheres of acetylene in a stirring autoclave for about 30 hours at about 40° C. 1 molecular proportion of acetylene is absorbed for each molecular proportion of amine used. The reaction product consisting of two layers is worked up in a similar manner to that described in Example 3.

There is obtained a yield of about 70 per cent of alpha-phenyl-alpha-N-dimethyl-propargylamine of the constitution:



having a boiling point of 69° C at 1 millimeter (mercury gauge) and also a small amount of the disubstituted acetylene.

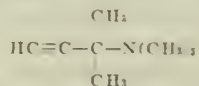
Example 6

36.5 parts of diethylamine and 2.5 parts of cuprous chloride which have previously been mixed with an equal amount of kieselguhr by powerful shaking are added in a pressure-tight vessel to a mixture of 33 parts of glacial acetic acid and 50 parts of 30 per cent formaldehyde while cooling. A mixture of 1 part of nitrogen and 2 parts of acetylene is then pressed in at 40° C under 15 atmospheres' pressure and the acetylene used up is replaced until the pressure no longer decreases. About 12 parts of acetylene are necessary for saturation.

The reaction product is freed from catalyst by filtration and then rendered alkaline with caustic soda solution and extracted with ether several times. The combined ether extracts are dried with sodium hydroxide and distilled. After removing the ether, the N-diethyl-propargylamine formed passes over at 120° C as a colorless liquid.

Example 7

A mixture of 290 parts of acetone, 20 parts of absolute alcohol in which 1 part of metallic sodium has been dissolved, 250 parts of 100 per cent dimethylamine and 10 parts of cuprous chloride is treated with acetylene in a stirring autoclave at about 80° C in the manner described in Example 1 until acetylene is no longer absorbed. After cooling and degasifying the dissolved acetylene and distilling off unchanged acetone and dimethylamine, there is obtained in a good yield the N-dimethyl-alpha-dimethylpropargylamine of the constitution:



The new compound melts at from 97° to 98° C, complete sublimation already taking place.

Example 8

22.5 parts of dimethylamine and an intimate mixture of 2 parts of cuprous chloride, 0.02 parts of silver nitrate and 2 parts of kieselguhr (as catalyst) are introduced into a mixture of 33 parts of glacial acetic acid and 50 parts of 30 per cent formaldehyde in a pressure-tight vessel while cooling. The whole is treated at room temperature with a mixture of 10 atmospheres of 10

acetylene and 5 atmospheres of nitrogen. After 7 hours, 13.5 parts of acetylene have been absorbed. The dimethyl-propargylamine formed is set free by the addition of caustic soda solution. It is extracted with ether, dried with caustic potash and then distilled.

WALTER REPPE.
ERNST KEYSSNER.
OTTO HECHT.

ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCT AND METHOD OF PREPARING SAME

Mathias Pier, Heidelberg, and Friedrich Christmann, Ludwigshafen - on - Rhine, Germany;
vested in the Alien Property Custodian

No Drawing. Application filed April 29, 1942

The present invention relates to the production of improved oils for lubricating purposes and, especially of low pour point oils.

We have found that the setting point of oils is lowered by the addition of even small amounts of products which are obtainable by the condensation of oxygen derivatives of aliphatic hydrocarbons of high molecular weight above 170, preferably more than 200, in which the oxygen is connected by two linkages with a carbon atom which in turn is in direct combination with only one further carbon atom, together with other organic compounds, advantageously cyclic hydrocarbons or olefines or mixtures of these substances.

As the oxygen derivative initial material may be mentioned acid chlorides of carboxylic acids having a molecular weight above 200, in particular fatty acids, such as stearic acid, oleic acid, palmitic acid and montanic acid, or the corresponding anhydrides, or keto acids. Oxidation products, containing carboxyl groups, of paraffin waxes are also suitable.

Of special advantage are the acid chlorides which are prepared in the usual manner by treatment of the acids or their salts with agents capable of replacing organic hydroxy groups by chlorine, for example thionyl chloride, phosgene, sulphuryl chloride, phosphorus oxychloride, phosphorus trichloride or phosphorus pentachloride. The acid chlorides are then condensed in the presence of condensing agents such as aluminum chloride, zinc chloride, iron chloride, boron fluoride, phosphorus oxychloride, active aluminum or zinc dust.

The temperatures employed for the condensation preferably range between 30 and 120° C and the condensation is preferably carried on to such an extent that the final condensation products have a molecular weight of more than 1000.

The condensation is advantageously carried out in the presence of substances having a condensing action and presenting a large inner surface, such as bleaching earths or active silica, in admixture with said other condensing agents. The condensation products may also be subjected to a subsequent treatment with these substances. In some cases, as for example, when using agents having a strong condensing action, it is preferable to carry out the reaction with the simultaneous addition of compounds retarding the reaction, such as zinc oxide, soda, calcium carbonate or ammonia.

Said acid chlorides are condensed with solid or liquid hydrocarbon products, such as tars, mineral oils, their distillation, extraction and cracking products or destructive hydrogenation products of carbonaceous materials. It is of especial advantage to employ those comprising hydrocarbons of unsaturated character; liquid olefines which have been obtained from paraffinic hydrocarbons, for example by cracking, may be em-

ployed. The condensation is advantageously effected with cyclic hydrocarbons. As such may be mentioned in particular naphthalene or other mineral coal tar fractions, such as crude benzene, middle oil or anthracene oil, as well as other products of an aromatic nature such as are obtained for example by destructive hydrogenation, preferably at temperatures of the upper part of the temperature range suitable for this reaction which treatment is called "aromatization", or by dehydrogenation. Olefines, such as ethylene, propylene or butylene, in the form of cracking gases may also be brought into reaction during the condensation.

The condensation products obtained according to the present invention have the appearance and the consistency of waxes.

The amounts of the resulting products to be added for the purpose of reducing the setting point may vary within wide limits, as for example between 0.1 and 10 per cent. Even lubricating oils, gear oils or gear grease having very high setting points are considerably improved by the addition. The condensation products prepared according to the present invention may be added to the lubricating oils also in larger amounts, as for example in amounts of 20 or 30 or 40 per cent or even more, whereby the viscosity index of the said oils is considerably improved.

The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples. The parts are by weight.

Example 1

Stearic acid is converted, by treatment with thionyl chloride at 80° C, into stearic acid chloride. 100 parts of the latter are dissolved in 100 parts of illuminating petroleum and, after the addition of 20 parts of naphthalene and 7 parts of aluminum chloride, are kept at about 30° C for 24 hours, and then for from about 1 to 2 hours at 90° C. The resulting condensation product is freed from aluminum chloride by centrifuging and distilled in vacuo. 35 parts of a waxy product are obtained as the distillation residue. If this be added in an amount of 0.5 per cent to a German machine oil having a setting point of 0° C, the setting point is lowered by about 25° C.

Example 2

95 parts of a gear oil are mixed with 5 parts of a synthetic oil prepared as described in Example 1. In this manner a gear oil is produced which remains soft or liquid even at low temperatures, whereby the lubricating capacity of the gear oil as well as its capacity of facilitating the control of the driving gear is increased.

This application is a division of application Serial No. 666,542, filed April 17, 1933.

MATHIAS PIER,
FRIEDRICH CHRISTMANN,

